Matrix Diffusion Toolkit

USER'S MANUAL

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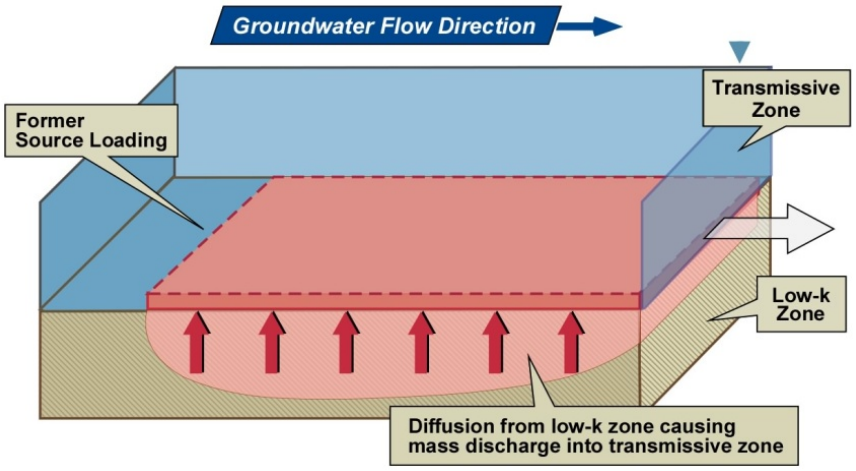

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MATRIX DIFFUSION TOOLKIT

Environmental Security Technology Certification Program

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QUICK START

Matrix Diffusion?

Low-k zones (i.e., low permeability zones such as silt, clay layers) can serve as indirect, low-level sources of contamination to transmissive zones due to matrix diffusion. If you can apply several simplifying assumptions about heterogeneity at your site coupled with its concentration history, the Matrix Diffusion Toolkit (Toolkit) can provide planning-level estimates of:

- mass discharge (sometimes called mass flux, in grams per day) and/or concentrations in the transmissive zone caused by matrix diffusion; and
- mass of contaminants and concentrations in the low-k zone.

Why is this important?

Understanding and evaluating matrix diffusion can provide information regarding a variety of key questions, such as:

1. If I remediate a transmissive zone, but my remediation technology doesn't remove contaminants from low-k zones in contact with the transmissive zone, will I be able to achieve my cleanup standards?
2. How much mass could be present in low-k zones at my site?
3. If I install a permeable reactive barrier, will I have trouble achieving cleanup standards downgradient of the barrier?
4. If I remove all the DNAPL, is there a chance I'll still be above MCLs?
5. How much longer might I have to wait for a source zone to achieve MCLs after the DNAPL is all gone?

Do I need special sampling data from the low-k zones?

If you want to learn more about the potential impacts of matrix diffusion, or want planning-level modeling results, then the Toolkit can be applied without sampling data from the low-k zones. The Toolkit can provide useful information about the *general* trends or style of matrix diffusion effects, but *absolute* values of the simulated results may vary considerably from actual field observations. The accuracy of the modeling results will be increased if there are data from the low-k zones that can be used to calibrate the Toolkit models.

How accurate are the results?

The two models utilized in the Toolkit are very simplified representations of an extremely complicated process and field conditions. Therefore, even with sampling data from the low-k zones, we consider the potential results as an "order-of-magnitude" range accuracy. But at many sites, this level of accuracy will still provide very useful information for site managers.

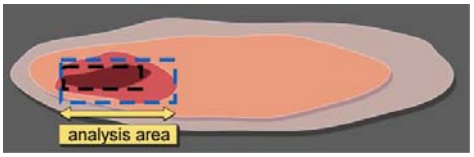
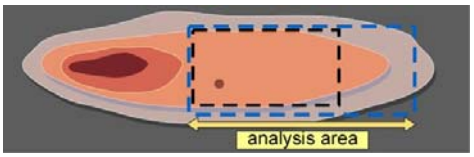
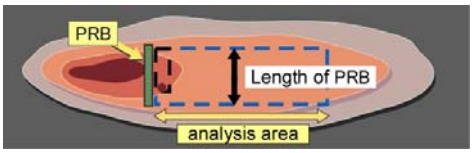
What input data will I need?

Some of the input data are similar to what is used for existing solute transport models, e.g., Darcy groundwater velocity, size of the modeled area, information on when the source started, etc. Other input data may appear new to many users; for example, you'll need to estimate the tortuosity of the low-k materials where matrix diffusion has occurred, diffusion coefficients, fraction organic carbon of the clays and silts being modeled, etc. The Toolkit provides default values and advice on how to pick the best value that represents your site conditions.

How is site data converted to a simple configuration that can be modeled with the Toolkit? What concentrations do I enter?

First, you pick which of two separate diffusion models to run (see Page 11). The Toolkit then guides you through how to set up the selected model. For example, to determine the modeled area length and width for the SRM, you can either enter your own length and width directly, or use the following method based on a historical contour map (see SRM Data Entry Step 5):

Contour Line Method: *Draw a downgradient transect line perpendicular to groundwater flow and an upgradient transect line perpendicular to groundwater flow to define the area you want to see results for from the Toolkit. Here are three examples where you need to enter the length and width of the black box and blue box in the drawing:*

Type of Problem to be Analyzed Using the Toolkit	Black Box in Drawing	Blue Box in Drawing
To see matrix diffusion impacts in a source zone: 	The Black Box is drawn around the highest concentration contour in the source area.	The Blue Box is drawn around the second highest concentration contour in the source area.
To see matrix diffusion impacts in a downgradient plume: 	The Black Box is drawn around the highest concentration contour downgradient of the source area.	The Blue Box is drawn around the second highest concentration contour downgradient of the source area.
To see matrix diffusion impacts downgradient of a Permeable Reactive Barrier (PRB): 	The Black Box is drawn around the highest concentration contour downgradient of the PRB.	The Blue Box is drawn around the second highest concentration contour downgradient of the PRB. The width of the box is the width of the PRB.

Both models assume a two-layer configuration, where a plume in a transmissive zone is in contact with a low-k zone. The loading period (where contaminants diffuse from the transmissive zone into the low-k zone) has to be estimated, followed by a release period (where contaminants diffuse from the low-k zone into the transmissive zone). One of the key challenges for running the Toolkit is coming up with good estimates for the year the loading period started and year the release period started.

In addition, a "loading concentration" is required to run the model. This is the concentration in the modeled area (the boxes described on the previous page) from the time the source started until the loading period ended. This is often before the time any groundwater monitoring wells were installed, and determining this value can be difficult. We recommend two ways to estimate the historical loading concentration:

1. Historical Process Information: At some sites, you might have certain process knowledge about the modeling area during the loading period, such as this area had DNAPL or there was a release of a certain strength waste. In this case, estimate the historical groundwater concentrations based on this information (such as the effectively solubility of the contaminant in a DNAPL) and use this as the Loading Concentration.

2. Highest Observed Concentration: More commonly, you will not have process knowledge, and in that case we recommend you use the highest observed concentration from a groundwater monitoring point in the modeled area (the two boxes) as a starting

point. While not perfect, this method is based on real data and represents observed loading concentrations in the modeled area.

Many sites have more than one low-k layer in contact with the plume. You can simulate this heterogeneity outside of the Toolkit using the default two-layer, one-interface configuration, and then multiplying the mass discharge from the Toolkit by the number of interfaces (the number of contacts between a transmissive zone and low-k zone) (see Inset 1 on page 10). You can do the same for concentration output if each interface intersects the screen of the assumed monitoring well.

Can the Toolkit be used with fractured rock sites?

The Toolkit is primarily designed for unconsolidated sites with two layers, a transmissive zone and a low-k zone. Although it can be used for fractured rock sites, the application and interpretation will require additional interpretation and expertise. The model basically assumes a single transmissive zone (which would be a fracture) and a single low-k zone (the rock matrix). To apply this to a fractured system, the mass discharge and concentration would have to be multiplied by two to account for the contribution from both sides of the fracture. To simulate multiple fractures, you would have to multiply the results from a single fracture by the number of fractures contributing to the mass flux/mass discharge at the point of interest.

What contaminants can be modeled with the Toolkit?

To date, most of the research involving matrix diffusion for low-k zones has focused on chlorinated solvents such as TCE (trichloroethene) and methyl-tert butyl ether (MTBE). However, in theory matrix diffusion processes should apply to almost any dissolved contaminant, including benzene and the other aromatic compounds found in gasoline, although the overall impacts may differ. Matrix diffusion of dissolved metals and radionuclides could also be modeled if a simplifying assumption of linear sorption/desorption relationship and no degradation can be applied.

Can the Toolkit be used at LNAPL sites?

In theory many of the processes at chlorinated solvent sites will be applicable to LNAPL sites. However, we are not aware of any detailed research studies where matrix diffusion at LNAPL source zones was evaluated. In addition, some LNAPL components may persist for a long period of time, making it difficult to understand whether the hydrocarbon plume is being sourced by matrix diffusion or from the persistent LNAPL phase. Note that one group documented matrix diffusion effects associated with a MTBE/TBA plume (Rasa et al., 2011), but this was not in an LNAPL source area.

Is the Toolkit able to simulate degradation in the low-k zone?

Not at this time. Numerical problems prevented a full implementation of the Dandy-Sale Model with degradation (Sale et al., 2008b), consequently, this version of the Toolkit assumes no degradation in the low-k zone. However, we hope to incorporate this feature in future versions of the Toolkit.

INTRODUCTION

Over the past several years, the groundwater research community in North America has become increasing aware that ***matrix diffusion*** has the potential to sustain dissolved contaminant concentrations in groundwater after the source is removed (e.g., Chapman and Parker, 2005; AFCEE, 2007; Sale *et al*., 2008a) or after remediation removes or isolates contamination from transmissive compartments. This persistent contaminant concentration can occur in the source zone itself, or in some cases, in the plume downgradient of the source (Figure 1).

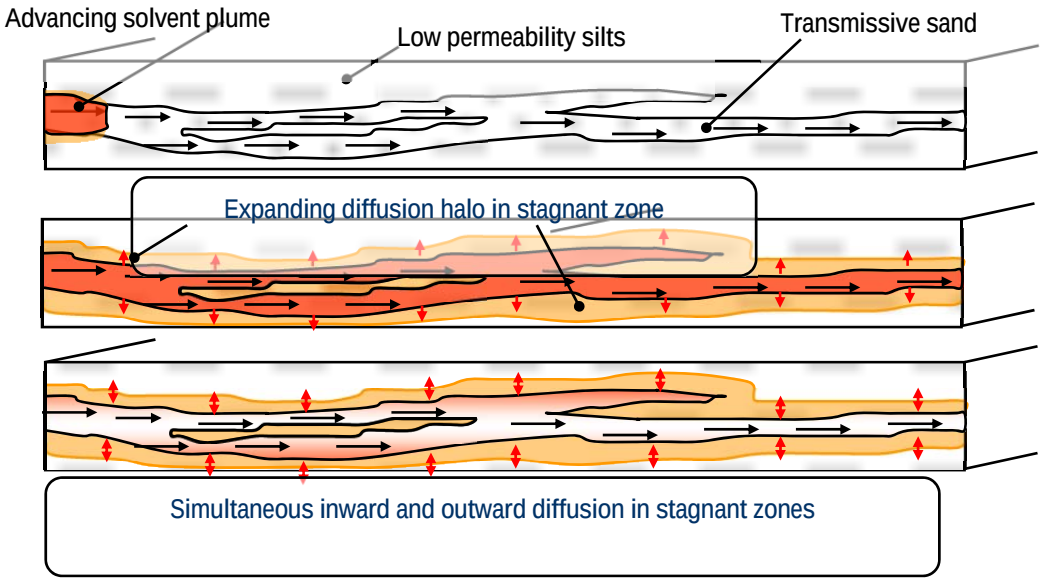


Figure 1: Conceptual model of matrix diffusion effects as part of plume response. (Source: T. Sale, T. Illangasekare, AFCEE, 2007)

The potential for matrix diffusion effects can be seen at virtually any site with heterogeneity in the subsurface, dense non-aqueous phase liquid (DNAPL), and/or where persistent groundwater contaminant concentrations after source-zone remediation have been observed. While matrix diffusion has been identified as a potential problem, there are relatively few tools available to help practitioners in the field determine if matrix diffusion could be a problem at their site. Currently, the field methods are still based on research techniques that are relatively expensive (i.e., drilling, collecting soil samples, etc.). There are site factors (i.e., high heterogeneity, low groundwater flow rate, high contaminant solubility, etc.) which can be evaluated to qualitatively estimate if matrix diffusion effects are expected to be significant. However, current analytical fate and transport models (such as BIOCHLOR and REMChlor) or complex numerical models (such as MODFLOW/MT3D) cannot accurately simulate matrix diffusion effects.

Some simple equations have been developed as part of an Air Force Center for Engineering and the Environment (AFCEE) research project (AFCEE, 2007) that can take some of the key conditions (presence of a low-k compartment, contaminant solubility, groundwater velocity, sorption, and time since the release occurred) and make quantitative predictions about the concentration and/or mass discharge that may remain in groundwater after all other source terms are removed. In other words, these

equations (a simple mass discharge model and a more sophisticated analytical solution) can be used to help answer these questions:

- What is the potential contaminant concentration in the source zone after the source material in the transmissive compartment is largely removed?
- What is the potential contaminant concentration downgradient in the plume after the source is removed or isolated (such as with a slurry wall or Permeable Reactive Barrier)?

To better equip the groundwater community with accessible, useable, and practical models for evaluating matrix diffusion effects, the Environmental Security Technology Certification Program (ESTCP) of the U.S. Department of Defense (DoD) has funded the development of this Matrix Diffusion Toolkit.

Based on the Microsoft Excel® platform, the Toolkit is an easy-to-use, comprehensive, free software tool that can assist site personnel to effectively and efficiently estimate what effects matrix diffusion will have at their site, and transfer the results to stakeholders. Furthermore, the software can assist project managers in determining if remediation goals are achievable in the short-term. The Toolkit can be applied to virtually any site with heterogeneity in the subsurface, DNAPL, and/or where persistent groundwater contaminant concentrations have been observed after source-zone remediation.

The Toolkit provides a valuable tool for developing site conceptual models, supporting site characterization efforts, planning remedial designs, and determining if matrix diffusion will affect remediation goals for groundwater sites. The software can assist site personnel in updating or creating a more accurate conceptual site model, which will enable them to determine if matrix diffusion processes are significant enough to cause "rebounding" of downgradient plume concentrations above remediation goals after plume remediation or isolation is complete. Having this information available before a remedy is implemented could assist site stakeholders in selecting more appropriate remedies and effectively and efficiently addressing the potential issues of matrix diffusion with regulators. Furthermore, addressing extended remediation time frames caused by matrix diffusion would lead to savings in project costs.

The Toolkit provides the following tools to calculate and evaluate matrix diffusion effects:

1) Square Root Model

A module to provide planning-level estimates of the mass discharge (in units of grams per day) caused by release from a low-k diffusion-dominated unit (typically silt or clay) into a high permeability advection-dominated unit (typically sand or gravel). Estimates of concentration and mass remaining in the high permeability unit, after the source is removed, are also provided.

2) Dandy-Sale Model

A module allowing users to perform: 1) contaminant transport via advection and transverse diffusion in the transmissive layer, and 2) transport via transverse diffusion in the low-k zone. The module provides planning-level estimates of:

Low-k Zone:

i) Aqueous, sorbed, and total concentration; and

ii) Aqueous, sorbed, and total mass.

Transmissive Zone:
i) Aqueous, sorbed, and total concentration;
ii) Aqueous, sorbed, and total mass; and
iii) Mass discharge.

3) Matrix Diffusion Related Tools

An additional feature that provides a review of theory and methods related to matrix diffusion:

a. *NAPL Dissolution Calculator:* a module that estimates the transverse diffusion of contaminants into the groundwater passing over the top of a Non-aqueous Phase Liquid (NAPL) pool and the transverse diffusion of contaminants into the low-k unit underlying the pool;
b. *Plume Magnitude Information:* a summary of the Plume Magnitude Classification System (Newell *et al*., 2011) and its application to site investigation and remediation;
c. *Low-k Zone Remediation Alternatives:* a summary of current alternatives for the remediation of low-k zones; and
d. *14-Compartment Model:* a discussion on the quantitative application of the 14-Compartment Model (Sale *et al*., 2008a).

The Matrix Diffusion Toolkit was developed for the ESTCP by GSI Environmental Inc., Houston, Texas, in conjunction with Colorado State University, Fort Collins, Colorado.

INTENDED USES FOR MATRIX DIFFUSION TOOLKIT AND LIMITATIONS

The **Matrix Diffusion Toolkit** attempts to assist site managers and site consultants better understand matrix diffusion and help site stakeholders determine if matrix diffusion processes are significant enough to cause "rebounding" of downgradient plume concentrations above remediation goals after plume remediation or isolation is complete. Having this information readily available before a remedy is implemented, could assist site stakeholders select more appropriate remedies and improve effective risk communication with regulators and the public.

The Toolkit is intended to be used in two ways:

1. **As a screening level tool for simulating matrix diffusion effects.** The Toolkit brings key technical resources, easy-to-use calculation worksheets, and case studies together into one easy-to-access platform.

    a. In addition, the Toolkit provides two methods for analyzing uncertainty in the estimation of mass discharge, concentration, and mass using the Square Root Model module. One option (performed automatically) provides a lower range, mostly likely value, and an upper range for estimated outputs based on the specified source area concentrations.

    The second option (Advanced Uncertainty Analysis) utilizes a Monte Carlo-type approach to analyze uncertainty in the actual concentration, porosity, apparent tortuosity factor exponent, and retardation factor measurements. With this tool, groundwater practitioners can estimate the accuracy of the hydrologic measurements that are being used for the matrix diffusion calculation.

    b. The Toolkit can also be used to estimate the diffusion of contaminants into the groundwater passing over the top of a NAPL pool and the diffusion of contaminants into the low-k unit underlying the pool.

2. **As a tool for learning about matrix diffusion.** The Toolkit reviews emerging methodologies associated with site characterization and matrix diffusion, such as the 14-Compartment Model (Sale *et al*., 2008a) and the Plume Magnitude Classification System (Newell *et al*., 2011).

The Toolkit has the following assumptions and limitations:

- Assumes the user is familiar with basic groundwater transport and mass balance concepts.

- Uses a simplified conceptual model of a two-layer aquifer system (a transmissive layer and a low-k layer) where there are two different time periods:
    - A **loading period** where there is a constant concentration of contaminants in the transmissive zone that drives contaminants into the low-k zone; and

  - A **release period**, where the transmissive zone is assumed to have no concentration and an upper-range estimate of release out of the low-k zone is generated.
  - That is, the system is assumed to be of the "on-off" type, with a defined "loading period" that extends for a certain period of time, that then switches to a "release period", where any concentration in the transmissive zone that originates from non-back-diffusion sources is instantly switched off.

- Assumes an infinitely thick low-k zone, which in practice means the low-k zone is at least **1 meter thick** for sites where matrix diffusion has been occurring for several decades. Thinner low-k zones can be modeled, but with more uncertainty in the final results. Case Studies 2A and 2B show both models in the Toolkit being applied to a tank study with layers as thin as 0.03 meters where the theoretical penetration in the low-k zones during the 124-day test period was about 0.25 meters. Despite not corresponding to the assumption of a low-k zone that is thicker than the penetration depth, the model outputs were within an order of magnitude of the actual measured concentrations from the tank study.

- Assumes no degradation in the low-k zone.

- To run the Monte Carlo analysis, users need to estimate what type of statistical distribution best fits the input data and what values best describe the distribution. In many cases data will be unavailable to make these estimates, so the user may have to rely on scientific/engineering judgment to use the Monte Carlo analysis.

- The Monte Carlo analysis cannot account for plume data that are not part of the monitoring system. Actual mass discharge, concentration, and mass values can be outside the reported range of mass flux values from the Monte Carlo analysis (for example, if new data show high concentration zones that were not captured by the original monitoring network).

- The Square Root model assumes an unimpeded release during the release period. In other words, for purposes of calculating the rate at which contaminants diffuse out of the low-k zones, the model assumes there is no concentration in the transmissive zone. Because diffusion from a low-k zone is a relatively weak force compared to active DNAPL sources, and because the model assumes an instantaneous switch from loading to release period, this assumption should not prevent the model from providing useful, order-of-magnitude type information.

- The Square Root model assumes that the loading of the low-k zone is a horizontal area directly over the low-k zone. This assumption can be applied to source zones (such as ones that contained DNAPL pools) or to downgradient parts of the plume (where a high-concentration aqueous phase plume provided the loading to the low-k zone).

- The Dandy-Sale model basically assumes the source zone is a vertical plane, and only estimates the effect of matrix diffusion downgradient of this plane. In

other words, the Dandy-Sale model only models matrix diffusion downgradient of a source zone.

- Concentration results from both the Square Root Model and Dandy-Sale Model are based on estimates of mass discharge leaving the low-k zone. Concentrations are then calculated by assuming a 10-foot screened interval. The 10-foot screened interval was selected because at an actual field site, contamination diffusing from a low-k zone might spread vertically above a 1-foot screen. It was thought to be very unlikely that there would be more than 10 feet of vertical spreading in the transmissive zone. Bottom line: the 10-foot screened interval is hard-wired into the models and cannot be changed by the user.

FREQUENTLY ASKED QUESTIONS

Why is matrix diffusion important? Won't the DNAPL take so long to go away that matrix diffusion will never be that important?

Matrix diffusion can be a key process both at sites where remediation has not been conducted, and at sites where much of the DNAPL has been removed by active remediation projects:

- For the no remediation case, a simple modeling study of a 675 kg DNAPL release showed that it would take about 39 years for the DNAPL to dissolve away naturally, and then it would take another 87 years until matrix diffusion went below a certain source strength (0.1 grams per day) (Seyedabbasi *et al*., 2012). This helps support the contention that there are a number of "Late Stage" chlorinated solvent sites where DNAPL is a relatively small part of the source, and matrix diffusion is the predominate contributor (Sale *et al*., 2008a,b). Obviously if there is a very large DNAPL release of hundreds of thousands of pounds, then DNAPL will likely be a large part of the site conceptual model for a long period of time.

- For the remediation case, there are perhaps thousands of sites where active in-situ remediation has removed DNAPL from the transmissive zone, but has left behind contaminants in the low-k zones. These sites are likely to be dominated by matrix diffusion effects now or sometime in the near future.

What is a low-k zone? Do I have these zones at my site?

Based on her research program at the University of Guelph, Dr. Beth Parker has a rule of thumb indicating that matrix diffusion can be an important process if there is a plume in a transmissive zone that is in contact with adjacent zones that have permeabilities lower than by a factor of 100 or more. In other words, if a contaminant plume moving in a 10^{-3} cm/sec sand is in contact with a 10^{-5} cm/sec silt, then the silt can be charged up with contaminants during a loading period (when concentrations in the sand are higher than the silt) and then slowly discharge contaminants into the sand via diffusion when the silt has higher concentrations than the sand.

The models in the Toolkit are based on simplifying assumptions, and one of the most important is the mathematical assumption that you have an infinitely thick low-k zone (in other words you can't input the thickness of your low-k zone). In practice that means the low-k zone should be at least **1 meter thick** for sites where matrix diffusion has been occurring for several decades. Thinner low-k zones, such as thin lenses and stringers, can be modeled, but with more uncertainty in the final results.

If you are dealing with thin units (less than 3 meters thick), you should check to see If your particular combination of input data (low-k layer thickness, retardation factor, source loading start, source removed, and see result time are the key factors) results in a problem by running the Dandy-Sale model. If this model showed a lot of contaminant mass has penetrated into the assumed infinitely thick low-k zone farther than the actual thickness of the low-k zone at your site, then your simulation will likely deviate from

reality at some point in time. However, if most of the mass is shallower than the thickness you observe in the field then the simulation should work reasonably well. Overall, sites with very thin clay stringers and/or lenses may be difficult to simulate unless the timeframes are very short.

What does the Matrix Diffusion Toolkit do?

Low-k zones can serve as indirect, low-level sources of contamination to transmissive zones due to matrix diffusion. If you can apply several simplifying assumptions about heterogeneity and a site's concentration history to your site, the Toolkit can tell you:

- the mass discharge (sometimes call mass flux, in grams per day) leaving the modeled area due to release from the low-k zones;
- the concentration of contaminants in a monitoring well with a 10-foot screen located in the transmissive zone in the downgradient portion of the modeled area;
- the average concentration of contaminant leaving the source zone assuming some minimum flow zone above the modeled low-k zone;
- the mass of contaminants in the low-k zone at any time; and
- the concentration of contaminants anywhere in the low-k zone at any time.

What questions can I address with the Matrix Diffusion Toolkit?

The Toolkit can be used to provide information regarding a variety of questions, such as:

1. If I remediate a transmissive zone, but my remediation technology doesn't remove contaminants from low-k zones in contact with the transmissive zone, will I be able to achieve my cleanup standards?

2. How much mass could be present in low-k zones at my site?

3. If I install a permeable reactive barrier, will I have trouble achieving downgradient cleanup standards?

4. If I remove all of the DNAPL, is there a chance I'll still be above MCLs?

5. How much longer might I have to wait for a source zone to achieve MCLs after all of the DNAPL is gone?

Because of the simplifying assumptions discussed above, results provided by the Toolkit will be planning-level information. But, these results can help you think about these different questions and tell you what might happen.

What if I don't have a two-layer system at my site? Can I still use the Matrix Diffusion Toolkit?

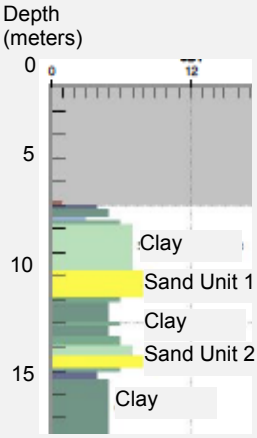
Yes, with some limitations. If you have multiple, thick, low-k units within a transmissive zone, you can determine the number of layers and multiply the model outputs by that number (see Inset 1 on the next page). Case Study 2 shows an example of a four-layer system with eight interfaces (two for each layer) that was modeled successfully with the Toolkit. Because both models in the Toolkit assume a single-layer, two-interface problem, the final concentration results from the Toolkit were multiplied by *eight* to get an estimate of the effect of all eight interfaces on concentration. The end results were concentrations that matched measured concentration output from the tank study to within an order of magnitude.

Do I need sampling data from the low-k zones to run the Toolkit models?

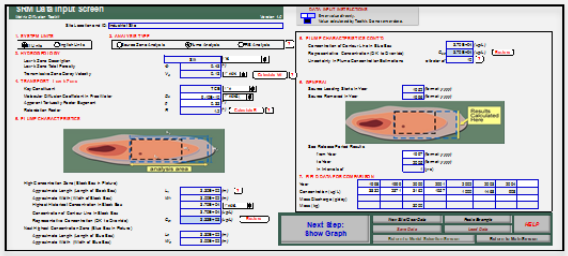
If you want results with a high level of confidence, then calibrating the Toolkit output to soil concentration data you collect from the low-k zones would be very important. However, if you want to learn more about the potential impacts of matrix diffusion, or want planning-level modeling results, the Toolkit can be run without data from the low-k zones.

INSET 1

HOW DO I GO FROM THIS …



TO THIS?



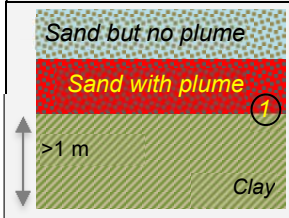
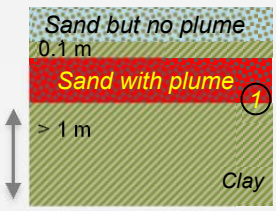
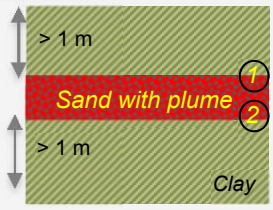
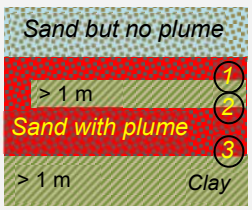
Basic Idea:

Step 1: Count the number of interfaces where a silt or clay layer, that is at least 1-meter thick, is in contact with the plume in transmissive sands/gravels. For the example above, if there was a plume in the yellow Sand Unit 1 between 10 and 12 meters, there would **be two interfaces** (both the clays above and below Sand Unit 1 are at least 1-meter thick; the model cannot simulate very thin clay stringers or lenses. See the FAQs).

Step 2: Run either model in the Toolkit, and get the result you are interested in: mass discharge (grams per day), mass (kilograms), or concentration in a well (mg/L).

Step 3: Multiply the results in Step 2 by the number of interfaces from Step 1. For example, if the Toolkit determines your simulation has a mass discharge of 2 grams per day (gpd) and you have 2 interfaces, the end result is a mass discharge of 4 gpd for your site. Similarly, if the Toolkit determines the concentration is 0.51 mg/L and you have 3 interfaces, the actual concentration is 1.53 mg/L.

See the four examples below for further details.

			
Plume in transmissive zone in contact with 1 interface. Low-k unit is > 1 meter thick. Number of Interfaces: 1	Plume in transmissive zone in contact with 2 interfaces, but top one is very thin and can't store much mass. Don't count top low-k layer. Number of Interfaces: 1	Plume in transmissive zone in contact with 2 interfaces, both low-k units > 1 meter thick. Count both interfaces. Number of Interfaces: 2	Plume of same concentration in transmissive zone in contact with 3 interfaces, all low-k units > 1 meter thick. Number of Interfaces: 3
Use Toolkit results with no adjustment.	**Use Toolkit results with no adjustment.**	**Multiply all Toolkit results by 2.**	**Multiply all Toolkit results by 3.**

How accurate are the results?

The two models utilized in the Toolkit are very simplified representations of an extremely complicated process and field conditions. Therefore, even with sampling data from the low-k zones, we consider the potential results as an "order-of-magnitude" range accuracy. But at many sites, this level of accuracy will still provide very useful information for site managers.

What input data will I need?

Some of the input data are similar to what is used for existing solute transport models (e.g., Darcy groundwater velocity, size of the modeled area, information on when the source started, etc.) Other input data will look new to many users, for example, you'll need to estimate the tortuosity of the low-k materials where matrix diffusion has occurred, diffusion coefficients, and fraction organic carbon of the clays and silts being modeled, etc. The Toolkit provides default values and advice on selecting representative values for your site conditions.

Can the Toolkit be used for fractured rock sites?

Yes, but the application and interpretation will require additional interpretation and expertise. The model basically assumes a single transmissive zone (which would be a fracture) and a single low-k zone (the rock matrix). To apply this to a fractured system, the mass discharge and concentration would have to be multiplied by two to account for the contribution from both sides of the fracture. To simulate multiple fractures, you would have to multiply the results from a single fracture by the number of fractures contributing to the mass flux / mass discharge at the point of interest.

What contaminants can be modeled with the Toolkit?

To date, most of the research involving matrix diffusion processes for low-k zones has focused on chlorinated solvents such as TCE (trichloroethene) and Methyl-tert butyl ether (MTBE). However, in theory, matrix diffusion processes should apply to almost any dissolved contaminant, including benzene and other aromatic compounds found in gasoline, although the overall impacts may differ. Matrix diffusion of dissolved metals and radionuclides can also be modeled if a simplifying assumption of a linear sorption/desorption relationship and no degradation can be applied.

Is the Toolkit able to simulate degradation in the low-k zone?

Not at this time. Numerical problems prevented a full implementation of the Dandy-Sale Model with degradation (Sale *et al.*, 2008b). Consequently, this version of the Toolkit assumes no degradation in the low-k zone. However, we hope to incorporate this feature in future versions of the Matrix Diffusion Toolkit.

Which model in the Toolkit should I choose: the Square Root Model or the Dandy-Sale Model?

I Want the Following Information:	Which Model?	Output
1. Mass Discharge (sometimes called mass flux) data from a low-k zone to a transmissive zone in units of grams per day vs. time (both past and future).	Square Root OR Dandy-Sale	Mass discharge vs. time plot
2. How much mass could be present in low-k zones at my site?	Square Root OR Dandy-Sale	Mass in low-k zone vs. time plot
3. If I install a permeable reactive barrier, will I have trouble achieving downgradient cleanup standards?	Square Root OR Dandy-Sale	Concentration* vs. time plot or mass discharge vs. time plot
4. If I remove all the DNAPL in a source zone, is there a chance I'll still be above MCLs? How much longer might I have to wait for a source zone to achieve MCLs after all DNAPL is gone?	Square Root OR Dandy-Sale (but SRM would simulate a more accurate source representation)	Concentration* vs. time plot or mass discharge vs. time plot
5. I want to know the concentration vs. depth profile in a low-k zone.	Dandy-Sale	Concentration* vs. depth plot or Concentration vs. lateral distance plot
6. I want to make sure the matrix diffusion model accounts for contaminant concentrations in the transmissive zone when calculating the release from low-k zones.	Dandy-Sale	Concentration* vs. time plot or mass discharge vs. time plot
7. I want to account for the travel time of the plume in the transmissive zone so that the loading period for the downgradient low-k zones starts later than the loading period for the near-source low-k zones. (This is more important for plumes with long residence times, > 20 years).	Dandy-Sale	Concentration* vs. time plot or mass discharge vs. time plot

** Concentration assuming a monitoring well with a 10-foot screened interval (this cannot be changed in the model).*

What are the key input data for the Square Root Model in the Toolkit?

The Square Root Model, originally based on work performed by Drs. Beth Parker and John Cherry, and modified by Dr. Tom Sale, asks you to provide these input data:

1. What is the **length and width of each zone**? You get to model two zones with different sizes and different concentrations. See the Data Input Section for examples of how to determine the length and width of the two zones.
2. How long (years) was the **loading period** (when concentrations in the transmissive zone were higher than the low-k zones)? This is based on your understanding of site history, such as the time from the initial release to the time when remediation was (or will be) performed on the transmissive zone.
3. What was the concentration during the loading period? It is rare to have monitoring data from the time of the release to now, so we've provided some guidance based on the maximum concentration ever observed in the zones you are modeling (see SRM Data Entry Step 5).
4. How **long (years) has release from low-k zones been occurring**? In other words, how long has it been since the transmissive zone concentration was lower than the concentrations that have diffused into the low-k zones? For sites where remediation has or will occur, this is easy: just enter the date when remediation reduced the concentrations in your modeling zones. For other situations, you can make some estimates to get an idea of the impact of matrix diffusion.
5. What is the **diffusion coefficient** for the contaminant of interest? The Toolkit provides a library of diffusion coefficients for the most common contaminants we deal with at sites.
6. What are the key transport properties of the clay: **tortuosity and retardation factor**? The Toolkit provides a calculator for you to estimate these parameters if you are not familiar with them.

What are the key input data for the Dandy-Sale Model in the Toolkit?

The Dandy-Sale Model is more sophisticated than the Square Root Model, and requires additional input data. However, it is based on the same conceptual model of a two-layer system and a loading period followed by a release period.

Can I calibrate the matrix diffusion models in the Toolkit?

Yes, but with the caution that groundwater monitoring data may represent a combination of residual contaminants from the original source (even if the source has been remediated) and from matrix diffusion. So a careful evaluation of the field data that you would calibrate against is necessary to make sure you aren't calibrating to the wrong values. See *Square Root Model Data Entry* and *Dandy-Sale Model Data Entry* for more information on how to calibrate the models.

How does the Toolkit handle uncertainty?

For the Square Root Model, we suggest that the Toolkit results are within an order of magnitude (a factor of 10). While this seems a large range, the results will provide useful information in context of the wide range of concentrations and mass discharge found in source zones (e.g., see the paper: "Contaminant Plume Classification System Based on Mass Discharge" by Newell *et al*., 2011). So, the model obtains information about whether you think the loading concentration has been stable or decreasing over time, and then applies a multiplier to give a range around the most likely value.

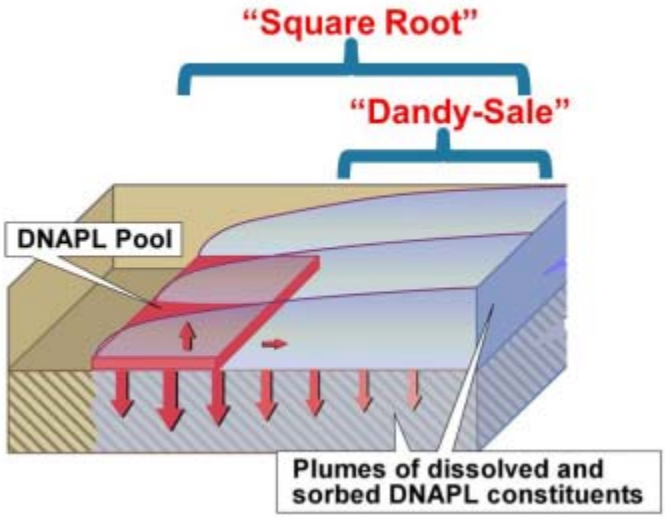
The Square Root Model also utilizes a Monte Carlo-type approach to analyze uncertainty in the actual concentration, porosity, apparent tortuosity factor exponent, and retardation factor measurements. With this tool, groundwater practitioners can estimate the accuracy of the hydrologic measurements that are being used for the matrix diffusion calculation.

The Dandy-Sale Model is likely to have the same level of accuracy as the Square Root Model. Because of the complexity of this model, we currently don't show the ± order of magnitude results in the model output.

Of course, with more field data (especially sampling results from the low-k zone) the accuracy of the modeling results will increase.

MATRIX DIFFUSION TOOLKIT MODELS

Two models are utilized in the Toolkit: the Square Root Model and the Dandy-Sale Model.



Square Root Model (SRM)

Building on work originally performed by Drs. Beth Parker and John Cherry, and modified by Dr. Tom Sale, the Square Root Model (SRM) provides planning-level estimates of the mass discharge (in units of grams per day) caused by release from a low-k diffusion-dominated unit (typically silt or clay) into a high permeability advection-dominated unit (typically sand or gravel). The Toolkit also estimates concentration and mass remaining in the high permeability unit after source removal.

Governing equations and assumptions are provided in Appendix A.1. Guidelines for selecting key input parameters for the model are outlined in Square Root Model Data Entry. For help on results, see Square Root Model Results.

Dandy-Sale Model (DSM)

Through a 2003 AFCEE project (Sale *et al*., 2008b), Dr. David Dandy at Colorado State University developed an exact analytical solution for a two-layer scenario shown in Figure 2. Key attributes of the model include contaminant transport via advection and transverse diffusion in the transmissive layer, transport via transverse diffusion in the low-k zone, unique retardation factors for each layer, unique contaminant degradation rates for each layer, and an adjustable source term.

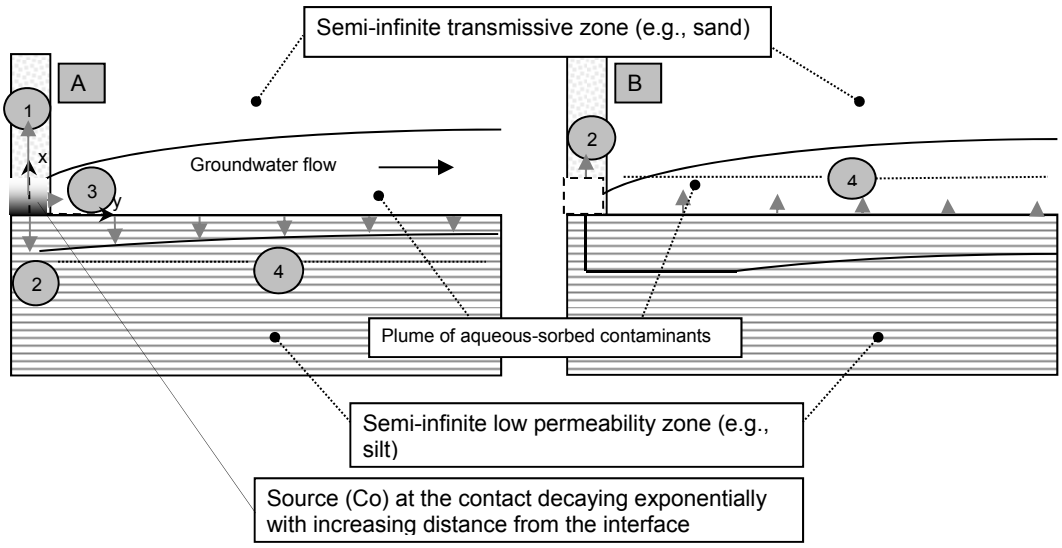


Figure 2: A conceptual model of the two-layer scenario. A) Active source – c_o at the contact decaying exponentially into the transmissive layer. B) Depleted source – source strength = 0 (from Sale *et al*., 2008b).

The theoretical basis for the module is discussed in Appendix A.2. Guidelines for selecting key input parameters for the model are outlined in Dandy-Sale Model Entry. For help on results, see Dandy-Sale Model Results.

Uncertainty Analysis

Uncertainty in mass flux estimates is a key issue in simulations of groundwater systems. The Toolkit provides two options for analyzing this uncertainty. One option (performed automatically) provides a lower range, most likely value, and an upper range for estimated outputs based on the specified source area concentrations.

The second option (Advanced Uncertainty Analysis) utilizes a Monte Carlo-type approach to analyze uncertainty in the actual source concentration, porosity, apparent tortuosity factor exponent, and retardation factor measurements. With this tool, groundwater practitioners can estimate the accuracy of the hydrologic measurements that are being used for the matrix diffusion calculation.

Monte Carlo analysis is a method of analyzing and quantifying uncertainties in model outputs due to the uncertainties in the input parameters (Rong *et al.*, 1998). Monte Carlo analysis refers to a computer-based system that uses random numbers from a probability distribution to obtain an approximation for the parameter of interest (USEPA, 1997; Bergin and Milford, 2000).

In the standard Monte Carlo approach, simple random sampling and a large number of runs (typically 100 to 1000) are required to obtain a meaningful probability distribution for the parameter. For each run of the standard approach, a random number is generated for the source concentration, porosity, apparent tortuosity factor exponent, and retardation factor entered by the user. This set of random inputs is then used to estimate concentration, mass discharge, and mass. Repeating this procedure a large

number of times yields a probability distribution from which statistical characteristics such as mean, percentile, and variance can be obtained. The Toolkit employs 1000 iterations for the Monte Carlo analysis.

Guidelines for selecting key input parameters for the model are outlined in Uncertainty Analysis.

SQUARE ROOT MODEL DATA ENTRY

SRM Data Input Screen
SRM Results
Advanced Uncertainty Analysis

Three important considerations regarding data input are:

1) To see the example dataset in the input screen of the software, click on the *Paste Example* button on the lower right portion of the input screen. The example dataset used in the Toolkit is obtained from Chapman and Parker (2005).
2) Because the Toolkit is based on an Excel® spreadsheet, you have to click outside of the cell where you just entered data or hit *Return* before any of the buttons will function. Additionally, **REMOVING OR ADDING** rows or columns in input screens may cause the program to crash.
3) Parameters used in the model are to be entered directly into the white/blue cells.

NOTE: Although literature values are provided, site-specific hydrogeologic, transport, and plume characteristic values will likely provide better results. If literature values are used and there is uncertainty in the value chosen, sensitivity analyses should be conducted to determine the effects of the uncertainty on model predictions.

Recommendations regarding calibrating (fitting) the SRM to actual field data

After the model has been set up and run, model output can be compared to actual field data from monitoring wells using either a concentrations comparison or a mass discharge comparison. Most times, the initial run will not produce modeled data that match field data. Considerations and recommended steps to improve the fit of simulated to field data are provided below.

The first caveat associated with calibrating the SRM is that the model assumes the original source zone is completely cleaned up and does not account for any residual source. In other words, at many sites, the concentrations from matrix diffusion may only be causing part of the contaminant concentrations in monitoring wells; residual mass from the source zone may also be contributing to the observed concentrations. Consequently, an exact match to observed concentration in a monitoring well should not be attempted if there is any uncertainty in matrix diffusion processes being the sole source of contaminants in the modeled zone.

In cases where a good comparison between concentrations and/or mass discharge from actual groundwater monitoring data can be made (either because there is no residual source or the matrix diffusion signal can be abstracted out), the recommended sequence of model input values to change is:

a. First, change the "representative concentrations" (C_{s1} and C_{s2}) in the black box and blue box, respectively. If the simulated concentrations are higher than observed concentrations, reduce the representative concentrations in the black and blue boxes.
b. If it is still difficult to get a good fit, try changing either the start or end of the loading period if there is some uncertainty on the exact years of these two times. To increase the simulated concentration, move the start of the loading period back in time or the start of the release period more recent in time. In other words, more time for diffusion during the loading period will result in higher concentrations during the release periods.
c. To further improve the match, after working with the previous two steps, consider changing some of the hydrogeologic and/or transport properties such as Darcy velocity, low-k zone tortuosity, and low-k zone retardation factor. Other parameters in the model can also be changed to develop a better match.

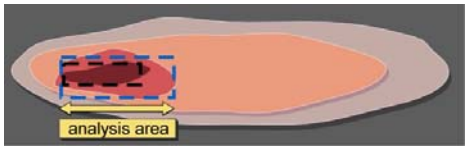
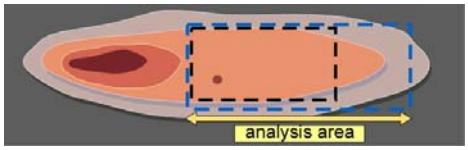
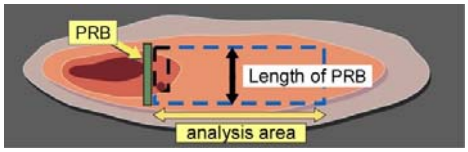
Because of the simplifying assumptions in the model, and the early state of matrix diffusion modeling in general, we consider the two models in the Toolkit to be an order of magnitude (a factor of 10) level of accuracy tools. While this seems a large range, the results will provide useful information in context of the wide range of concentrations and mass discharge found in source zones (for example, see the paper: "Contaminant Plume Classification System Based on Mass Discharge" by Newell *et al*., 2011). This level of accuracy means that there is probably no need to spend considerable effort in trying to calibrate the models to the 2nd or 3rd significant digit.

SRM Data Input Screen:

Step 1: *System Units*

PARAMETER	SYSTEM UNITS
Description	Unit system to perform matrix diffusion calculations in.
Units	SI System (meters, etc.) or English Units (feet, etc.).
How to Enter Data	Choose the appropriate radio button.

Step 2: *Analysis Type*

PARAMETER	ANALYSIS TYPE
Description	Type of matrix diffusion analysis to perform. **Select "Source Zone Analysis"** to see matrix diffusion impacts in a source zone:  **Select "Plume Analysis"** to see matrix diffusion impacts in a downgradient plume:  **Select "PRB Analysis"** to see matrix diffusion impacts downgradient of a PRB: 
How to Enter Data	Choose the appropriate radio button.

Step 3: *Hydrogeology*

PARAMETER	LOW-k ZONE DESCRIPTION
Description	Description of the low-k zone.
How to Enter Data	Choose from drop down list or enter directly.

PARAMETER	LOW-k ZONE TOTAL POROSITY (Φ)
Units	Unitless.
Description	Dimensionless ratio of the volume of voids to the bulk volume of the surface soil column matrix, but excluding secondary porosity (fractures, solution cavities, etc.). *Total porosity* is the ratio of all voids (including non-connected voids) to the bulk volume of the aquifer matrix. Effective porosity and any porosity data with secondary porosity information should not be used.
Typical Values	The model input screen has these default values: Clay 0.47 (mid-range of values below) Silt 0.48 (mid-range of values below) Sandstone/shale 0.10 (Pankow and Cherry (1996), Table 12.2) Fractured Sandstone 0.08 (Pankow and Cherry (1996), Table 12.2) Granite 0.006 (Pankow and Cherry (1996), Table 12.2) Values for total porosity from Domenico and Schwartz (1990), in part from Davis (1969), and Johnson and Morris (1962): **SEDIMENTARY** Porosity (-) Gravel, coarse 0.24 - 0.36 Gravel, fine 0.25 - 0.38 Sand, course 0.31 - 0.46 Sand, fine 0.26 - 0.53 Silt 0.34 - 0.61 Clay 0.34 - 0.60 **SEDIMENTARY ROCKS** Sandstone 0.05 - 0.30 Siltstone 0.21 - 0.41 Shale 0 - 0.10 **CRYSTALLINE ROCKS** Dense crystalline rocks 0 - 0.05 Koerner (1984) reports these values for unit weight for saturated soils (note no dry bulk density values are reported for these materials): Glacial till, very mixed grain: 0.20 Soft glacial clay: 0.57 Stiff glacial clay: 0.37 Soft slightly organic clay: 0.66 Soft very organic clay: 0.75 Soft bentonite: 0.84 One fractured microcrystalline limestone in Virginia had matrix porosities ranging from 0.0004 to 0.0065 (GSI Environmental).
Source of Data	Typically estimated. Occasionally obtained through physical property testing of site soil samples.
How to Enter Data	Enter directly. (Note that if the low-k zone description is selected from the drop down list, the Toolkit provides a default value for the parameter.)

PARAMETER	TRANSMISSIVE ZONE DARCY VELOCITY (V_d)
Units	cm/sec, ft(or m)/day, ft(or m)/yr.
Description	Transmissive zone groundwater Darcy velocity. To characterize concentrations in a well with a 10-foot screened interval in the transmissive layer, representative measurements are required for the Darcy velocity (or both the hydraulic flow gradient and the hydraulic conductivity) of the flow system. Representative measurements of the Darcy velocity should be obtained at one or more locations, using appropriate slug or pumping test methods. In the SRM, Darcy velocity is only used for calculation of concentration from the mass discharge output.
Typical Values	0.2 - 200 ft/yr (0.06 - 61 m/yr). (Newell *et al*., 1996.)
Source of Data	Calculated by multiplying hydraulic conductivity by hydraulic gradient ($V_d = K \times i$). Use of actual site data for hydraulic conductivity and hydraulic gradient parameters is strongly recommended.
How to Enter Data	1) Select units and enter directly, or 2) Calculate by pressing the "Calculate Vd" button and entering values for: a) Hydraulic conductivity, and b) Hydraulic gradient.

PARAMETER	TRANSMISSIVE ZONE HYDRAULIC CONDUCTIVITY (K)
Units	cm/sec, ft(or m)/day, ft(or m)/yr.
Description	Measure of the permeability of the transmissive layer. To characterize concentrations in the transmissive layer, representative measurements are required for the Darcy velocity (or both the hydraulic flow gradient and the hydraulic conductivity) of the flow system. Representative measurements of the hydraulic conductivity of the transmissive layer should be obtained at one or more locations using appropriate slug test or pumping test methods (Newell *et al*., 2003).
Typical Values	Silts: $1x10^{-6}$ - $1x10^{-3}$ cm/s Silty sands: $1x10^{-5}$ - $1x10^{-1}$ cm/s Clean sands: $1x10^{-3}$ - 1 cm/s Gravels: > 1 cm/s (Newell *et al*., 1996.)
Source of Data	Pump tests or slug tests at the site. It is strongly recommended that actual site data be used for all matrix diffusion evaluations.
How to Enter Data	1) Select units, and 2) Enter directly.

PARAMETER	TRANSMISSIVE ZONE HYDRAULIC GRADIENT (i)
Units	ft/ft (or m/m).
Description	The slope of the potentiometric surface. In unconfined aquifers, this is equivalent to the slope of the water table.
Typical Values	0.0001 - 0.1 ft/ft (0.0001 - 0.1 m/m).

Source of Data	Calculated by constructing potentiometric surface maps using static water level data from monitoring wells and estimating the slope of the potentiometric surface.
How to Enter Data	Enter directly.

Step 4: *Transport – Low-k Zone*

PARAMETER	KEY CONSTITUENT
Description	Constituent of interest.
How to Enter Data	Enter directly or choose from drop down list.

PARAMETER	MOLECULAR DIFFUSION COEFFICIENT IN FREE WATER (D_o)
Units	cm^2/sec, m^2/sec.
Description	A factor of proportionality representing the amount of substance diffusing across a unit area through a unit concentration gradient in unit time.
Typical Values	Benzene 9.8E-06 cm^2/s; Ethylbenzene 7.8E-06 cm^2/s; Toluene 8.6-06 cm^2/s; Xylene 8.5E-06 cm^2/s; MTBE 9.4E-05 cm^2/s; Tetrachloroethene 8.2E-06 cm^2/s; Trichloroethene 9.1E-06 cm^2/s; cis-1,2-Dichloroethene 1.1E-05 cm^2/s; Vinyl Chloride 1.2E-05 cm^2/s; 1,1,1-Trichloroethane 8.8E-06 cm^2/s (TRRP, 2008) (Note that there is a wide range of reported values; for example, Wiedemeier *et al*. (1999) report a D_o for benzene of 1.1E-05 cm^2/s.) For more information see Pankow and Cherry, 1996 (for solvents) and Wiedemeier *et al*., 1999 (variety of constituents).
Source of Data	Chemical reference literature such as Pankow and Cherry, 1996 (for solvents); Wiedemeier *et al*., 1999 (variety of constituents); or other references with chemical properties.
How to Enter Data	1) Select units, and 2) Enter directly. (Note that if the constituent is selected from the drop down list, the Toolkit provides a value for the parameter.)

PARAMETER	APPARENT TORTUOSITY FACTOR EXPONENT (p)
Units	Unitless.
Description	The Apparent Tortuosity Factor (τ) relates the molecular diffusion coefficient in free water (D_o) of a constituent in a porous medium to its effective diffusion coefficient (D_e). Values of τ can range between 0 and 1. Estimations of τ can be obtained using the relationship: $$\frac{D_e}{D_o} = \tau \cong \emptyset^p$$ Where $\boldsymbol{\Phi}$ is the porosity and *p* the Apparent Tortuosity Factor Exponent. Depending on the geologic medium, values for *p* can vary between 0.3 and 5.4 (Charbeneau, 2000; Pankow and Cherry, 1996; Dullien, 1992; Lerman, 1979; and Millington and Quirk, 1961).

Typical Values	Clay: 1.33 Fractured Sandstone: 0.63 Granite: 0.57 Sandstone/Shale: 1 Silt: 0.33 (Payne *et al.*, 2008.)
Source of Data	Literature.
How to Enter Data	Enter directly. (Note that if the low-k zone description is selected from the drop down list, the Toolkit provides a value for the parameter.)

PARAMETER	**RETARDATION FACTOR (R)**
Units	Unitless.
Description	The retardation factor is the ratio of the dissolved plus sorbed constituent mass to the dissolved constituent mass in the aqueous phase in a unit volume of aquifer. The retardation factor is a function of both aquifer and constituent properties.
Typical Values	For transmissive zones, these retardation factors are commonly observed: 1 - 3 (typical for BTEX) 2 - 5 (typical for chlorinated solvents) It is thought that retardation factors for low-k zones are higher than transmissive zones. Currently, there are few sites where these values have been determined, however.
Source of Data	Usually estimated from soil and chemical data using the following expression: $R = 1 + K_d \cdot \rho_d / n$ where $K_d = K_{oc} \cdot f_{oc}$ and ρ_d = bulk density, n = porosity, K_{oc} = organic carbon-water partition coefficient, K_d = distribution coefficient, and f_{oc} = fraction organic carbon on uncontaminated soil. In some cases, the retardation factor can be estimated by comparing the length of a plume affected by adsorption (such as the benzene plume) with the length of a plume that is not affected by adsorption (such as chloride). Most plumes do not have both types of constituents, so it is more common to use the estimation technique. (See "fraction organic carbon" below for more information.)
How to Enter Data	1) Select units and enter directly, or 2) Calculate by pressing the "Calculate R" button and entering values for: a) Soil Bulk Density, and b) Distribution Coefficient or Fraction Organic Carbon and Organic Carbon Partitioning Coefficient.

PARAMETER	**SOIL BULK DENSITY OF LOW-k ZONE (rhob')**
Units	g/mL.
Description	Density of the saturated low-k zone (referred to as "soil"), excluding soil moisture.

Typical Values	Although this value can be measured in the lab, estimated values are used in most cases. A value of 1.7 g/mL is used frequently for unconsolidated media. Representative values in g/mL for specific geologic media are shown below (Lovanh *et al.*, 2000; derived from Domenico and Schwartz, 1990). Clay: 1.0 - 2.4 — Loess: 0.75 - 1.6 Sands-ne: 1.6 - 2.68 — Shale: 1.54 - 3.17 Limes-ne: 1.74 - 2.79 — Granite: 2.24 - 2.46 Basalt: 2 - 2.7 — Medium Sand: 1.34 - 1.81 Koerner (1984) reports these values in g/mL for unit weight for saturated soils (note no dry bulk density values are reported for these materials): Glacial till, very mixed grain: 2.32 — Soft glacial clay: 1.77 Stiff glacial clay: 2.07 — Soft slightly organic clay: 1.58 Soft very organic clay: 1.43 — Soft bentonite: 1.27
Source of Data	Either from an analysis of soil samples at a geotechnical lab or more commonly, application of estimated values such as 1.7 g/mL.
How to Enter Data	Enter directly.

PARAMETER	**LOW-k ZONE FRACTION ORGANIC CARBON (f'_{oc})**
Units	Unitless (gram per gram).
Description	Fraction of the aquifer material comprised of natural organic carbon in uncontaminated areas. More natural organic carbon means higher adsorption of organic constituents on the aquifer matrix.
Typical Values	Although based on limited data, 0.0002 - 0.10 for low-K zones is a likely range. But, some sites may be higher or lower. Examples: At the Moffatt Field site, the f_{oc} of the clay fraction is about 0.0066 (Roberts *et al.*, 1990). Domenico and Schwartz (1990) report these values: silt (Wildwood Ontario): 0.00102; from Oconee River sediment: coarse silt: 0.029; medium silt: 0.02; fine silt: 0.0226. Chapman and Parker (2005) report a f_{oc} of glaciolacustrine aquitard composed of varved silts and clays: 0.0024 to 0.00104 with an average of 0.00054. Adamson (2012) reports f_{oc} = 0.001 for a clay layer in Jacksonville, Florida and f_{oc} values for silts at the MMR site in Massachusetts ranging from <0.0005 to 0.0022 (median value = 0.0014) for one core using Leco carbon analyzer; a second core had f_{oc} values < 0.005 for 10 samples and two samples with 0.00067 and 0.00084 (gram per gram). Values for f_{oc} using Walkley-Black wet oxidation method were generally higher by a factor of 2 to 3. Values ranging from 0 to 0.078 have been reported for silts at the F.W. Warren site in Wyoming, with a median value of 0.
Source of Data	The fraction organic carbon value should be measured, if possible, by collecting a sample of aquifer material from an uncontaminated saturated zone and performing a laboratory analysis (e.g., ASTM Method 2974-87 or equivalent). If unknown, a default value of 0.002 should be used (twice the typical default of 0.001 value used for transmissive systems).
How to Enter Data	Enter directly.

PARAMETER	ORGANIC CARBON PARTITIONING COEFFICIENT (K_{oc})
Units	mL/g.
Description	Chemical-specific partition coefficient between soil organic carbon and the aqueous phase. Larger values indicate greater affinity of organic constituents for the organic carbon fraction of soil. This value is chemical specific and can be found in chemical reference books.
Typical Values	Tetrachloroethene 155 mL/g Trichloroethene 93 mL/g cis-1,2-Dichloroethene 29 mL/g Vinyl Chloride 11 mL/g 1,1,1-Trichloroethane 110 mL/g Benzene 66 mL/g Ethylbenzene 204 mL/g Toluene 140 mL/g Xylene 240 mL/g MTBE 14 mL/g (TRRP, 2008.) (Note that there is a wide range of reported values; for example, Mercer and Cohen (1990) report a K_{oc} for benzene of 83 mL/g.) For more information, see Pankow and Cherry, 1996 (for solvents) and Wiedemeier *et al*., 1999 (variety of constituents).
Source of Data	Chemical reference literature such as Pankow and Cherry, 1996 (for solvents); Wiedemeier *et al*., 1999 (variety of constituents); or other references with chemical properties. Alternatively, one can use relationships between K_{oc} and solubility or K_{oc} and the octanol-water partition coefficient (K_{ow}) to determine K_{oc}. A collection of values is presented in the Chemical Parameter Database included in this manual.
How to Enter Data	Enter directly. (Note that if the constituent is selected from the drop down list, the Toolkit provides a value for the parameter.)

Step 5: *Plume Characteristics*

Key point about modeling area and concentration: You do not need to model the *entire* source or plume area, but only the ones exposed to the highest historical concentrations. You can likely get 90% of the loading from matrix diffusion by modeling the area inside the two highest-concentration contour lines (as shown by the blue and black boxes in the figures below) on a historical plume map in the area of interest.

Two methods are provided for this Step. First time users are more likely to use the *Contour Map Method,* but skilled users will likely go straight to the *Standard Method.*

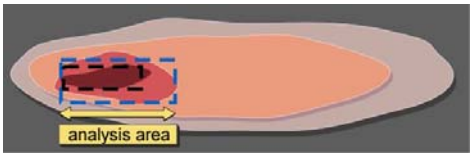
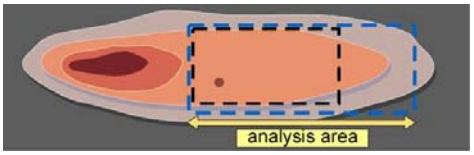
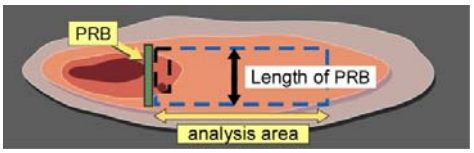
Standard Method: Determine the area you want to model for matrix diffusion and enter the length, width, and representative historical loading concentration. Note the model allows you to enter data for two different areas at your site (i.e., two lengths, two widths, and two representative loading concentrations).

Contour Map Method: Use a method based on lengths, widths, and concentrations from a historical contour map, preferably one with the highest historical concentrations observed during the monitoring record. For example, if source concentrations have been decreasing over time, use a concentration contour map from 1990 and not 2012.

Determining modeling length and width:

The first goal is to define a length, width, and loading concentration for the first modeled area (black box) and the second modeled area (blue box **excluding the black box area**). Here are two options for entering the data.

Step 5.1.
Standard Method: Enter your own length and width in the model.
Contour Map Method: Draw a downgradient transect line perpendicular to groundwater flow and an upgradient transect line perpendicular to groundwater flow to define the area you want to assess using the Toolkit. Here are three examples where you need to enter the length and width of the areas representing the source (black box and blue box) in the drawing:

Type of Problem to be Analyzed Using the Toolkit	Black Box in Drawing	Blue Box in Drawing
To see matrix diffusion impacts in a source zone: 	The Black Box is drawn around the highest contour in the source area.	The Blue Box is drawn around the second highest contour in the source area.
	Note: You want to use a contour map with the highest concentrations measured at the site to represent higher historical concentrations.	
To see matrix diffusion impacts in a downgradient plume: 	The Black Box is drawn around the highest contour downgradient of the source area.	The Blue Box is drawn around the second highest contour downgradient of the source area.
To see matrix diffusion impacts downgradient of a PRB: 	The Black Box is drawn around the highest contour downgradient of the PRB.	The Blue Box is drawn around the second highest contour downgradient of the PRB. The width of the box is the width of the PRB.

Step 5.2.
Standard Method: Enter your own length and width for the first modeled area (L_1 and W_1).
Contour Line Method: Find the highest concentration contour line on the historical plume map between the upgradient and downgradient transects (denoted by the **black box** in the Toolkit input screen figure). Estimate the area (in square feet or square meters) between these transects and inside this contour line. At most sites, you can get a "close enough" value by estimating the approximate width and approximate length of an equivalent area. Enter these into the Toolkit.

Step 5.3.
Standard Method: Enter your own length and width for the second modeled area (L_2 and W_2).
Contour Line Method: Find the second highest concentration contour line on the historical plume map between the upgradient and downgradient transects (denoted by the **blue box** in the Toolkit input screen figure). Estimate the area (in square feet or square meters) between these transects and inside this contour line. At most sites, you can get a "close enough" value by i) estimating the approximate width and ii) approximate length of an equivalent area. (The Toolkit will automatically subtract out overlapping areas.) If you don't want to use this second area, set the length, width, and concentration equal to the values for the black box in the SRM input screen.

Determining loading concentration:

A loading concentration is required to run the model for up to two modeled areas (the black box and the blue box on the input screen). This is the typical historical concentration in the modeled area (the boxes described on the previous page) from the time the source started until the loading period ended. This is often before the time any groundwater monitoring wells were installed. We provide two data sources and two methods that can be used to obtain loading concentrations:

Data Source 1. Site History or Process Information: Some sites might have available certain process knowledge about the modeling area during the loading period, such as this area had DNAPL or there was a release of a certain strength waste. In this case, estimate the historical groundwater concentrations based on this information (such as the effective solubility of the contaminant in a DNAPL) and use this as the Loading Concentration.

For example, the effective solubility of a constituent in a known DNAPL pool in the source could be used when modeling the source zone, or if the DNAPL in the pool was comprised of 50% Trichloroethene (TCE), a concentration of 550 mg/L (50% of TCE solubility of 1100 mg/L) could be used. Alternatively, one could use an estimate of the average historical concentration from the time the source started to the end of the loading period; sometimes a groundwater model with a source decay term (such as REMChlor (Falta et al., 2007)) can be used to estimate historical groundwater concentrations in the early period of a plume's life cycle.

Data Source 2. Highest Observed Concentration: More commonly, good Data Source 1 information will not be available. In that case, we recommend using the highest observed concentration from a groundwater monitoring point in the modeled area (the two boxes) and a groundwater concentration contour map from the period with the highest observed concentrations from the monitoring network. This is typically the oldest concentration contour map available. While not perfect, this method is based on real data and represents observed loading concentrations in the modeled area.

Step 5.4.
Standard Method: Skip this Step – all you need is the Representative Concentration (Step 5.6).
Contour Line Method: Determine the loading concentration using *Data Source 1* or *Data Source 2.* Use the maximum concentration from any well within the highest concentration contour (denoted by the **black** box in the Toolkit input screen figure). Your goal is to get a concentration that reflects historical conditions before the monitoring system was installed (at most sites).

Step 5.5.
Standard Method: Skip this Step – all you need is the Representative Concentration) C_{s1}) (Step 5.6).
Contour Line Method: Determine the concentration of the highest concentration contour (denoted by the **black** box in the Toolkit input screen figure, Step 5.2 above). Again, use a contour map from the highest concentration period where groundwater samples were collected.

Step 5.6.
Standard Method: Enter your "Representative Concentration" (loading concentration) (C_{s1}) directly for this first area using Data Source 1 or Data Source 2.
Contour Map Method: The Toolkit calculates the geometric mean of the highest historical concentration within the **black** box and the contour line representing the **black** box. This is the "Representative Concentration" during the loading period (abbreviated C_{s1}). You can override this value if you want, and just enter what you think is a good historical loading concentration for the black box area.

Step 5.7.
Standard Method: Skip this Step – all you need is the Representative Concentration (C_{s2}) (Step 5.6).
Contour Map Method: Determine the concentration of the next highest concentration contour line (from Step 5.3 above). (If the highest contour line is 100 mg/L), then use the 10 mg/L contour.)

Step 5.8.
Standard Method: Enter your "Representative Concentration" (loading concentration) (C_{s2}) directly for this second area using Data Source 1 or Data Source 2. If you don't want to use this second area, just set the concentration equal to the black box in the SRM input screen.
Contour Map Method: The Toolkit calculates the geometric mean of the highest historical concentration within the **blue** box and the contour line representing the **blue** box – this is the "Representative Concentration" during the loading period (abbreviated C_{s2}). You can override this value if you want, and just enter what you think is a good historical loading concentration for the blue box area.

PARAMETER	HIGH CONCENTRATION ZONE APPROXIMATE LENGTH (L_1)
Units	ft (m).
Description	Standard Method: You can model two separate areas and the Toolkit will combine the diffusion processes. This is the length of your first modeled area. Contour Map Method: Length of the highest concentration contour line on a historical plume map between the upgradient and downgradient transects that represent your modeled area (denoted by the **black box** in the Toolkit input screen figure).
Typical Values	0 - 3300 ft (0 - 1000 m).
Source of Data	Standard Method: Modeled area length for this first of two subareas. Contour Map Method: Contour map should be from the highest concentration period where groundwater samples were collected. For example, if concentrations have been decreasing, use a concentration contour map from 1990 and not 2012.
How to Enter Data	Enter directly.

PARAMETER	HIGH CONCENTRATION ZONE APPROXIMATE WIDTH (W_1)
Units	ft (m).
Description	Standard Method: You can model two separate areas and the Toolkit will combine the diffusion processes. This is the width of your first modeled area. Contour Map Method: Width of the highest concentration contour line on a historical plume map between the upgradient and downgradient transects that represent your modeled area (denoted by the **black box** in the Toolkit input screen figure).
Typical Values	0 - 3300 ft (0 - 1000 m).
Source of Data	Standard Method: Modeled area width for this first of two subareas. Contour Map Method: Contour map should be from the highest concentration period where groundwater samples were collected. For example, if concentrations have been decreasing, use a concentration contour map from 1990 and not 2012.
How to Enter Data	Enter directly.

PARAMETER	HIGHEST HISTORICAL CONCENTRATION IN BLACK BOX (C_{S1})
Units	ug/L or mg/L.
Description	Standard Method: Leave this blank and just enter the historical loading concentration for the first modeled area in "Representative Concentrations." Contour Map Method: The highest maximum observed concentration in the modeled area "black box" area defined by the length and width above.
Typical Values	0.0001 – 20,000 mg/L.
Source of Data	Standard Method: Not needed. Contour Map Method: Use a contour map from the highest concentration period where groundwater samples were collected. For example, if concentrations have been decreasing, use a concentration contour map from 1990 and not 2012.
How to Enter Data	Enter directly.

PARAMETER	CONCENTRATION OF CONTOUR LINE IN BLACK BOX
Units	ug/L or mg/L.
Description	Standard Method: Leave this blank and just enter the historical loading concentration for the first modeled area in "Representative Concentrations." Contour Map Method: Concentration of contour line represented by the **black box** in the Toolkit input screen figure.
Typical Values	0.0001 – 10,000 mg/L.
Source of Data	Standard Method: this is not needed. Contour Map Method: Use a contour map from the highest concentration period where groundwater samples were collected. For example, if concentrations have been decreasing, use a concentration contour map from 1990 and not 2012.
How to Enter Data	Enter directly.

PARAMETER	REPRESENTATIVE CONCENTRATION (C_{s1})
Units	ug/L or mg/L.
Description	Representative historical loading concentration of first modeled area, denoted by the **black box** in the Toolkit input screen figure. **This value is a key parameter that can be changed during the calibration process to increase or decrease the simulated mass discharge, concentration, or mass to better match field data** (see the beginning of this section).
Typical Values	0.0001 – 20,000 mg/L.
Source of Data	Standard Method: *Data Source 1. Site History or Process Information:* For example, the effective solubility of a constituent in a known DNAPL pool in the source could be used when modeling the source zone, or if the DNAPL in the pool was comprised of 50% Trichloroethene (TCE), a concentration of 550 mg/L (50% of TCE solubility of 1100 mg/L) could be used. Alternatively, one could use an estimate of the average historical concentration from the time the source started to the end of the loading period; sometimes a groundwater model with a source decay term (such as REMChlor (Falta et al., 2007)) can be used to estimate historical groundwater concentrations in the early period of a plume's life cycle. *Data Source 2. Highest Observed Concentration:* More commonly, good Data Source 1 information will not be available. In that case, we recommend using the highest observed concentration from a groundwater monitoring point in the modeled area (the two boxes) and a groundwater concentration contour map from the period with the highest observed concentrations from the monitoring network. This is typically the oldest concentration contour map available. While not perfect, this method is based on real data and represents observed loading concentrations in the modeled area. Contour Map Method: This is calculated automatically by the model from the previous data above as the geometric mean of highest historical concentration and the contour line concentration. You can override this value.
How to Enter Data	Enter directly or let the Toolkit calculate it. (Note that, if overwritten, the Toolkit calculated value in the blue cell can be replaced by pressing the "Restore" button.)

PARAMETER	NEXT HIGHEST CONCENTRATION ZONE APPROXIMATE LENGTH (L_2)
Units	ft (m).
Description	Standard Method: You can model two separate areas and the Toolkit will combine the diffusion processes. Enter the length of your second modeled area, or leave blank if you only want to model one area. Contour Map Method: Concentration of contour line denoted by the **blue box** in the Toolkit input screen figure.
Typical Values	0.001 - 500 ft (0.001 - 152 m).
Source of Data	Standard Method: Enter the length your 2nd modeled area. Leave blank if you are only modeling one area. Contour Map Method: Use a contour map from the highest concentration

	period where groundwater samples were collected. For example, if concentrations have been decreasing, use a concentration contour map from 1990 and not 2012.
How to Enter Data	Enter directly.

PARAMETER	NEXT HIGHEST CONCENTRATION ZONE APPROXIMATE WIDTH (W_2)
Units	ft (m).
Description	Standard Method: You can model two separate areas and the Toolkit will combine the diffusion processes. This is the width of your second modeled area. Contour Map Method: Width of the second highest concentration contour line on a historical plume map between the upgradient and downgradient transects that represent your modeled area (denoted by the **blue box** in the Toolkit input screen figure).
Typical Values	0 – 3,300 ft (0 – 1,000 m).
Source of Data	Standard Method: Modeled area width for this second of two subareas. Contour Map Method: Contour map should be from the highest concentration period where groundwater samples were collected. For example, if concentrations have been decreasing, use a concentration contour map from 1990 and not 2012.
How to Enter Data	Enter directly.

PARAMETER	CONCENTRATION OF CONTOUR LINE IN BLUE BOX
Units	ug/L or mg/L.
Description	Standard Method: Leave this blank and just enter the historical loading concentration for the first modeled area in "Representative Concentrations." Contour Map Method: Concentration of contour line denoted by the **blue box** in the Toolkit input screen figure..
Typical Values	0.0001 – 1,000 mg/L.
Source of Data	Standard Method: this is not needed. Contour Map Method: Use a contour map from the highest concentration period where groundwater samples were collected. For example, if concentrations have been decreasing, use a concentration contour map from 1990 and not 2012.
How to Enter Data	Enter directly.

PARAMETER	REPRESENTATIVE CONCENTRATION (C_{s2})
Units	ug/L or mg/L.
Description	Representative historical loading concentration of second modeled area, denoted by the **blue box** in the Toolkit input screen figure. **This value is a key parameter that can be changed during the calibration process to increase or decrease the simulated mass discharge, concentration, or mass to better match field data** (see the beginning of

	this section).
Typical Values	0 – 20,000 mg/L.
Source of Data	Standard Method: This could be the same sources of data used for Cs1 described earlier, but for a second part of the modeled area. Information from either Data Source 1 or Data Source 2 can be used. Contour Map Method: This is calculated automatically by the model from the previous data above as the geometric mean of highest contour line and second highest contour concentration. This value can be overwritten.
How to Enter Data	Enter directly or let the Toolkit calculate it. (Note that, if overwritten, the Toolkit calculated value in the blue cell can be replaced by pressing the "Restore" button).

PARAMETER	UNCERTAINTY IN PLUME CONCENTRATION ESTIMATIONS
Description	Users should make a realistic estimate on how much uncertainty is associated with the concentration estimation being modeled. The main point of this parameter (and the software to some extent) is that there is a high-level uncertainty in any source concentration estimation. A value of ± factor of 10 is typically used. Note that if a value of 1 is used, then only the "most likely" estimate line will be shown on the graphs.
How to Enter Data	Enter directly.

Step 6: *General*

PARAMETER	SOURCE LOADING STARTS IN YEAR
Units	Year (yyyy).
Description	Year source loading started. This is estimated from site historical records, and is almost always from the 1950s, 1960s, 1970s, or early 1980s. If the release was over a long period of time, usually it is better to enter the earliest year. **This can be used as a calibration parameter** (see the beginning of this section).
How to Enter Data	Enter directly.

PARAMETER	SOURCE REMOVED IN YEAR
Units	Year (yyyy).
Description	Year source was removed. This is either: 1) the year that best represents when concentrations in the middle of the modeled area were reduced significantly by source remediation; or 2) when source zone natural attenuation processes reduced the concentrations in the middle of the modeled area significantly. For example, the source could likely be considered removed by natural attenuation *for the purposes of this model* if the transmissive zone of the modeled area has been reduced by 90% or 99% compared to the historical all-time concentrations. **This can be used as a calibration parameter** (see the beginning of this section).
How to Enter Data	Enter directly.

PARAMETER	SEE RELEASE PERIOD RESULTS FROM YEAR
Units	Year (yyyy).
Description	Starting year for displaying matrix diffusion results.
How to Enter Data	Enter directly.

PARAMETER	SEE RELEASE PERIOD RESULTS TO YEAR
Units	Year (yyyy).
Description	Ending year for displaying matrix diffusion results.
How to Enter Data	Enter directly.

PARAMETER	SEE RELEASE PERIOD RESULTS IN INTERVALS OF
Units	yrs.
Description	Time intervals matrix diffusion results are calculated at.
How to Enter Data	Enter directly.

Step 7: *Field Data for Comparison*

PARAMETER	FIELD DATA FOR COMPARISON - YEAR
Units	Year (yyyy).
Description	Years in which field data are available for calibration. These data are displayed with model results in the *Next Step: Show Graph* option.
Source of Data	Monitoring wells located in the area of interest.

How to Enter Data	Enter directly.

PARAMETER	FIELD DATA FOR COMPARISON - CONCENTRATION
Units	ug/L or mg/L.
Description	Concentration measurements in transmissive zone area of interest. These data are displayed with model results in the *Next Step: Show Graph* option.
Typical Values	0.001 – 10,000 mg/L.
Source of Data	Monitoring wells located in the area of interest screened close to the low-k unit being modeled. To match model output, the actual monitoring wells in the field should have screens long enough to capture any of the contaminant mass diffusing off the low-k zone. In other words, if possible, you should use data from wells with 5- to 10-foot screened intervals, and not from shorter screened intervals.
How to Enter Data	Enter directly.

PARAMETER	FIELD DATA FOR COMPARISON – MASS DISCHARGE
Units	g/day.
Description	Mass discharge measurements in transmissive zone and/or low-k zone area of interest. These data are displayed with model results in the *Next Step: Show Graph* option. Low-k zone mass discharge should be entered as negative values.
Typical Values	0.001 - 10,000 g/d.
Source of Data	Transects of wells located in the area of interest, pumping well data, or flux meters.
How to Enter Data	Enter directly.

PARAMETER	FIELD DATA FOR COMPARISON – MASS
Units	kg.
Description	Mass measurements in transmissive zone area of interest. These data are displayed with model results in the *Next Step: Show Graph* option.
Typical Values	0.10 - 100,000 kg.
Source of Data	Soil samples located in the area of interest, pumping well data, calculated from groundwater data and saturated soil constituent concentration data, or estimated from NAPL relationships. Software tools such as SourceDK (Farhat *et al*., 2004) can be used to estimate mass.
How to Enter Data	Enter directly.

PARAMETER	NEXT STEP: SHOW GRAPH
Description	Proceeds to the results of matrix diffusion analysis.

PARAMETER	NEW SITE/CLEAR DATA
Description	Clears **ALL** data related to the SRM model in the Toolkit memory banks. Use this button to start a new project.

PARAMETER	PASTE EXAMPLE
Description	Clears **ALL** data related to the SRM model in the Toolkit memory banks and pastes an example dataset. The example dataset used in the Toolkit is obtained from Chapman and Parker (2005).

PARAMETER	SAVE DATA
Description	Saves all the SRM model data. **DO NOT ADD ANY EXTENSIONS TO FILE NAME WHEN SAVING**.

PARAMETER	LOAD DATA
Description	Loads data files saved through the Toolkit. **DO NOT EDIT ANY TOOLKIT FILES**. Editing files may cause the Toolkit to crash.

PARAMETER	RETURN TO MODEL SELECTION SCREEN
Description	Returns to the Model Selection Screen.

PARAMETER	RETURN TO MAIN SCREEN
Description	Returns to the Matrix Diffusion Toolkit Main Screen.

SRM Model Results

PARAMETER	SEE MASS DISCHARGE RESULTS
Description	Mass discharge from the entire low-k and transmissive zones in units of g/day. Negative mass discharge values represent diffusion into the low-k zone from the transmissive zone. Positive values represent release from the low-k zone into the transmissive zone. Note this mass discharge from the entire low-k zone is assumed to be transported instantaneously to the downgradient edge of the modeled area (there is no advection or travel time component of the Square Root Model). However, because diffusion from a low-k zone is typically much slower than the travel time in the transmissive zone (multiple decades vs. months or years), this approximation should not cause too much problem for most simulations. If travel time is an important part of the simulation, try using the DSM model. A lower range, most likely value, and an upper range for estimated outputs are provided, based on the input source area concentrations. The user may use the *Log←→Linear* button to see the results on a semi-log plot.

PARAMETER	WHAT'S UP WITH THE GAP?
Description	In this simple model, the mass discharge due to release from low-k zones in the first few seconds, hours, and days after the loading period ends is extremely high, but only lasts a short time. Consequently, to avoid confusion associated with these high-mass discharge spikes, a 1-yr gap (between the loading period termination and the start of the release period) is utilized in the output graph. Matrix diffusion is a long process (typically decades or more). Because the transition phase between the loading period and release period is a year or more at many sites (such as the case where remediation is performed), the missing year is not likely to be an issue for most matrix diffusion modeling projects.

PARAMETER	SEE CONC RESULTS
Description	Concentration in the transmissive zone from a monitoring well with a 10-foot screened interval. This value is calculated using the mass discharge results as described above. See the "Intended Uses and Limitations" Section for why the screen interval is hard-wired to be 10-foot long and not a user input. If you are sure all the mass discharge is being captured by a well with a different screened interval, you can get the modeled concentration in this well by multiplying the model output by the ratio of the screens (your screened interval ÷ 10 feet). A lower range, most likely value, and an upper range for estimated outputs are provided, based on the input source area concentrations. The user may use the *Log←→Linear* button to see the results on a semi-log plot.

PARAMETER	SEE MASS RESULTS
Description	Mass in the transmissive zone. A lower range, most likely value, and an upper range for estimated outputs are provided, based on the input source area concentrations. The user may use the *Log←→Linear* button to see the results on a semi-log plot.

PARAMETER	RUN ADVANCED UNCERTAINTY ANALYSIS
Description	Uncertainty in parameter estimates is a key issue in estimating matrix diffusion effects. The Toolkit provides two options for analyzing this uncertainty. One option (performed automatically) provides a lower range, mostly likely value, and an upper range for estimated outputs based on the specified source area concentrations. The second option (Advanced Uncertainty Analysis) utilizes a Monte Carlo-type approach to analyze uncertainty in the actual concentration, porosity, apparent tortuosity factor exponent, and retardation factor measurements. With this tool, groundwater practitioners can estimate the accuracy of the hydrologic measurements that are being used for the matrix diffusion calculation.

PARAMETER	SAVE DATA
Description	Saves all the SRM model data. ***DO NOT ADD ANY EXTENSIONS TO FILE NAME WHEN SAVING.*** ***Note that this option does not save any edits performed on the graphs by the user. To save such edits, use the save function of Excel® and save the entire Toolkit file.***

PARAMETER	RETURN TO SRM DATA INPUT
Description	Returns to the SRM data input screen.

PARAMETER	EXPORT/PRINT DATA TABLE
Description	Exports the time, mass discharge, mass, concentration, and plume magnitude information shown in the table into a text file for use in other programs. Prints the data table shown on the screen on the default printer. To print on a different printer, select the printer in the "Print" options in Excel® and then press the "Print" button.

PARAMETER	RETURN TO MAIN SCREEN
Description	Returns to the Matrix Diffusion Toolkit Main Screen.

Uncertainty Analysis: Perform Uncertainty Analysis

Uncertainty in parameter estimates is a key issue in estimating matrix diffusion effects. The Toolkit provides two options for analyzing this uncertainty.

One option (performed automatically) provides a lower range, mostly likely value, and an upper range for estimated outputs based on the specified source area concentrations.

The second option (Advanced Uncertainty Analysis) utilizes a Monte Carlo-type approach to analyze uncertainty in the actual concentration, porosity, apparent tortuosity factor exponent, and retardation factor measurements. With this tool, groundwater practitioners can estimate the accuracy of the hydrologic measurements that are being used for the matrix diffusion calculation.

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PARAMETER	ADVANCED UNCERTAINTY ANALYSIS (EVALUATE HOW UNCERTAINTY IN INPUT DATA AFFECTS TOTAL MASS FLUX)
Description	This module uses the Monte Carlo approach to analyze uncertainty in the actual concentration, porosity, apparent tortuosity factor exponent, and retardation factor measurements. In the Monte Carlo-type approach, a random number is generated for every value of concentration, porosity, apparent tortuosity factor exponent, and retardation factor entered by the user. This set of random inputs is then used to calculate mass discharge in both the low-k and transmissive zones, concentration in the transmissive zone, and mass in the transmissive zone. Repeating this procedure a large number times yields a probability distribution from which statistical characteristics such as mean, percentile, and variance can be obtained. The Toolkit performs 1000 iterations for the Monte Carlo approach.
How to Enter Data	*1)* Specify a probability distribution for each parameter (see Appendix A.3 of the User's Manual for details on probability distributions). The Toolkit assumes that the values entered in the Input screen are the mean values. *2)* For the normal distribution, specify the standard deviation as a percent of the mean. For lognormal distributions, specify the error factor, EF; (the ratio of the 95th percentile to the median of the lognormal data or the ratio of the median to the 5th percentile). (NOTE: the error factor MUST be greater than one). For uniform distribution, specify the lower and upper limits as percentages of the mean. *3)* Perform Input Uncertainty Analysis.

Uncertainty Analysis: Results

PARAMETER	SEE MASS DISCHARGE RESULTS
Description	The 5th percentile, median, and 95th percentile for mass discharge, based on the user's choice of interpolation method and uncertainty in the input variables as defined by their probability distributions, means, variances, and ranges. Negative mass discharge values represent diffusion into the low-k zone from the transmissive zone. Positive values represent diffusion from the low-k zone into the transmissive zone. The user may use the *Log←→Linear* button to see the results on a semi-log plot.

PARAMETER	SEE CONC RESULTS
Description	The 5th percentile, median, and 95th percentile for concentration from a well with a 10-foot screen in the transmissive zone, based on the user's choice of interpolation method and uncertainty in the input variables as defined by their probability distributions, means, variances, and ranges. The user may use the *Log←→Linear* button to see the results on a semi-log plot.

PARAMETER	SEE MASS RESULTS
Description	The 5th percentile, median, and 95th percentile for mass in the transmissive zone, based on the user's choice of interpolation method and uncertainty in the input variables as defined by their probability distributions, means, variances, and ranges. The user may use the *Log←→Linear* button to see the results on a semi-log plot.

PARAMETER	SAVE DATA
Description	Saves all the SRM model data. **DO NOT ADD ANY EXTENSIONS TO FILE NAME WHEN SAVING**. ***Note that this option does not save any edits performed on the graphs by the user. To save such edits, use the save function of Excel® and save the entire Toolkit file.***

PARAMETER	RETURN TO SRM RESULTS
Description	Returns to the SRM Model Results screen.

PARAMETER	RETURN TO SRM DATA INPUT
Description	Returns to the SRM data input screen.

PARAMETER	EXPORT UNCERTAINTY DATA
Description	Exports the time, mass discharge, concentration, and mass shown on the graphs into a text file for use in other programs.

PARAMETER	RETURN TO MAIN SCREEN
Description	Returns to the Matrix Diffusion Toolkit Main Screen.

DANDY-SALE MODEL DATA ENTRY

DSM Data Input Screen
DSM Results

Three important considerations regarding data input are:

1) To see the example dataset in the input screen of the software, click on the *Paste Example* button on the lower right portion of the input screen. The example dataset used in the Toolkit is obtained from Chapman and Parker (2005).
2) Because the Toolkit is based on an Excel® spreadsheet, you have to click outside of the cell where you just entered data or hit *Return* before any of the buttons will function. Additionally, **REMOVING OR ADDING** rows or columns in input screens may cause the program to crash.
3) Parameters used in the model are to be entered directly into the white/blue cells.

NOTE: Although literature values are provided, site-specific hydrogeologic, transport, and plume characteristic values will likely provide better results. If literature values are used and there is uncertainty in the value chosen, sensitivity analyses should be conducted to determine the effects of the uncertainty on model predictions.

Recommendations Regarding Calibrating (Fitting) the DSM to Actual Field Data

After the model has been set up and run, model output can be compared to actual field data from monitoring wells using either a concentrations comparison or a mass discharge comparison. Most times, the initial run will not produce modeled data that match field data. Considerations and recommended steps to improve the fit of simulated data to field data are provided below.

The first caveat associated with calibrating the DSM is that the model assumes the original source zone is completely cleaned up and does not account for any residual source. In other words, at many sites, the concentrations from matrix diffusion may only be causing part of the contaminant concentrations in monitoring wells. Consequently, an exact match to observed concentration in a monitoring well should not be attempted if there is any uncertainty in matrix diffusion processes being the sole source of contaminants in the modeled zone.

In cases where a good comparison between concentrations and/or mass discharge from actual groundwater monitoring data can be made (either because there is no residual source or the matrix diffusion signal can be abstracted out), the recommended sequence of model input values to change is:

1) First change the "Plume Loading Concentration" (C_0). If the simulated concentrations are higher than observed concentrations, reduce the representative concentrations.

2) If it is still difficult to get a good fit, try changing either the start or end of the loading period if there is some uncertainty on the exact years of these two times. To increase the simulated concentration, move the start of the loading period back in time or the start of the release period more recent in time. In other words, more time for diffusion during the loading period will result in higher concentrations during the release periods.

3) To further improve the match, after working with the previous two steps, consider changing some of the hydrogeologic and/or transport properties such as Darcy velocity, low-k zone tortuosity, and low-k zone retardation factor. Other parameters in the model can also be changed to develop a better match.

Because of the simplifying assumptions in the model, and the early state of matrix diffusion modeling in general, we consider the two models in the Toolkit to be an order of magnitude (a factor of 10) level of accuracy tools. Therefore, there is probably no need to spend considerable effort in trying to calibrate the models to the 2nd or 3rd significant digit. While this seems a large range, the results will provide useful information in context of the wide range of concentrations and mass discharge found in source zones (for example, see the paper: "Contaminant Plume Classification System Based on Mass Discharge" by Newell *et al*., 2011).

DSM Data Input Screen:

Step 1: *System Units*

PARAMETER	SYSTEM UNITS
Description	Unit system to perform matrix diffusion calculations in.
Units	SI System (meters, etc.) or English Units (feet, etc.).
How to Enter Data	Choose the appropriate radio button.

Step 2: *Hydrogeology*

PARAMETER	TRANSMISSIVE ZONE DESCRIPTION
Description	Description of the transmissive zone. Sand, gravel, and silt are provided as the three selections.
How to Enter Data	Choose from drop down list or enter directly.

PARAMETER	TRANSMISSIVE ZONE EFFECTIVE POROSITY (n_e)
Units	Unitless.
Description	Dimensionless ratio of the volume of voids to the bulk volume of the surface soil column matrix. Note that *total porosity* is the ratio of all voids (including non-connected voids) to the bulk volume of the aquifer matrix. Differences between total and effective porosity reflect lithologic controls on pore structure. In unconsolidated sediments coarser than silt size, effective porosity can be less than total porosity by 2-5% (e.g., 0.28 vs. 0.30) (Smith and Wheatcraft, 1993).
Typical Values	Toolkit default values provided are averages of the ranges below. Gravel 0.10 - 0.35 Coarse Sand 0.20 - 0.35 Fine Sand 0.10 - 0.30 Medium Sand 0.15 - 0.30 (From Wiedemeier *et al*., 1999; originally from Domenico and Schwartz, 1990; and Walton, 1988).
Source of Data	Typically estimated. Occasionally obtained through physical property testing of site soil samples. One commonly used value for silts and sands is 0.25. The ASTM RBCA Standard (ASTM, 1995) includes a default value of 0.38 (to be used primarily for unconsolidated deposits). A collection of default values is presented in the Geologic Parameter Database included in this manual.
How to Enter Data	Enter directly. (Note that if the transmissive zone description is selected from the drop down list, the Toolkit provides a default value for the parameter.)

PARAMETER	LOW-k ZONE DESCRIPTION
Description	Description of the low-k zone.
How to Enter Data	Choose from drop down list or enter directly.

PARAMETER	LOW-k ZONE TOTAL POROSITY (n')
Units	Unitless.
Description	Dimensionless ratio of the volume of voids to the bulk volume of the surface soil column matrix, but excluding secondary porosity (fractures, solution cavities, etc. *Total porosity* is the ratio of all voids (including non-connected voids) to the bulk volume of the aquifer matrix. Effective porosity and any porosity data with secondary porosity information should not be used.
Typical Values	The model input screen has these default values: Clay 0.47 (mid-range of values below) Silt 0.48 (mid-range of values below) Sandstone/shale 0.10 (Pankow and Cherry (1996), Table 12.2) Fractured Sandstone 0.08 (Pankow and Cherry (1996), Table 12.2) Granite 0.006 (Pankow and Cherry (1996), Table 12.2) Values for total porosity from Domenico and Schwartz (1990), in part from Davis (1969), and Johnson and Morris (1962): **SEDIMENTARY** Porosity (-) Gravel, coarse 0.24 - 0.36 Gravel, fine 0.25 - 0.38 Sand, course 0.31 - 0.46 Sand, fine 0.26 - 0.53 Silt 0.34 - 0.61 Clay 0.34 - 0.60 **SEDIMENTARY ROCKS** Sandstone 0.05 - 0.30 Siltstone 0.21 - 0.41 Shale 0 - 0.10 **CRYSTALLINE ROCKS** Dense crystalline rocks 0 - 0.05 Koerner (1984) reports these values for unit weight for saturated soils (note no dry bulk density values are reported for these materials): Glacial till, very mixed grain: 0.20 Soft glacial clay: 0.57 Stiff glacial clay: 0.37 Soft slightly organic clay: 0.66 Soft very organic clay: 0.75 Soft bentonite: 0.84 One fractured microcrystalline limestone in Virginia had matrix porosities ranging from 0.0004 to 0.0065 (GSI Environmental).
Source of Data	Typically estimated. Occasionally obtained through physical property testing of site soil samples.
How to Enter Data	Enter directly. (Note that if the low-k zone description is selected from the drop down list, the Toolkit provides a default value for the parameter.)

PARAMETER	TRANSMISSIVE ZONE SEEPAGE VELOCITY (V)
Units	cm/sec, ft(or m)/day, ft(or m)/yr.
Description	Actual interstitial groundwater velocity, equaling Darcy velocity divided by effective porosity.
Typical Values	1 - 1500 ft/yr (0.3 - 457 m/yr).
Source of Data	Calculated by multiplying hydraulic conductivity by hydraulic gradient and dividing by effective porosity ($V = (K \times i) / n_e$). It is strongly recommended that actual site data be used for hydraulic conductivity and hydraulic gradient data parameters; effective porosity can be estimated.
How to Enter Data	1) Select units and enter directly, or 2) Calculate by pressing the "Calculate V" button and entering values for: a) Hydraulic conductivity, and b) Hydraulic gradient.

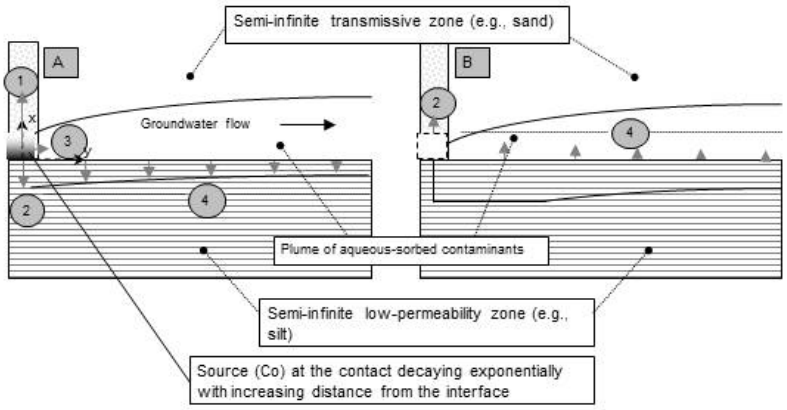
PARAMETER	TRANSMISSIVE ZONE HYDRAULIC CONDUCTIVITY (K)
Units	cm/sec, ft(or m)/day, ft(or m)/yr.
Description	Measure of the permeability of the transmissive layer. To characterize concentrations in the transmissive layer, representative measurements are required for the Darcy velocity (or both the hydraulic flow gradient and the hydraulic conductivity) of the flow system. Representative measurements of the hydraulic conductivity of the transmissive layer should be obtained at one or more locations using appropriate slug test or pumping test methods (Newell *et al*., 2003).
Typical Values	Silts: $1x10^{-6}$ - $1x10^{-3}$ cm/s Silty sands: $1x10^{-5}$ - $1x10^{-1}$ cm/s Clean sands: $1x10^{-3}$ - 1 cm/s Gravels: > 1 cm/s (Newell *et al*., 1996.)
Source of Data	Pump tests or slug tests at the site. It is strongly recommended that actual site data be used for all matrix diffusion evaluations.
How to Enter Data	1) Select units, and 2) Enter directly.

PARAMETER	TRANSMISSIVE ZONE HYDRAULIC GRADIENT (i)
Units	ft/ft (or m/m).
Description	The slope of the potentiometric surface. In unconfined aquifers, this is equivalent to the slope of the water table.
Typical Values	0.0001 - 0.1 ft/ft (0.0001 - 0.1 m/m).
Source of Data	Calculated by constructing potentiometric surface maps using static water level data from monitoring wells and estimating the slope of the potentiometric surface.

How to Enter Data	Enter directly.

Step 3: *Transport*

PARAMETER	KEY CONSTITUENT
Description	Constituent of interest.
How to Enter Data	Enter directly or choose from drop down list.

PARAMETER	PLUME LOADING CONCENTRATION IMMEDIATELY ABOVE LOW-k ZONE IN VERTICAL PLANE SOURCE DURING LOADING PERIOD (C_o)
Units	ug/L or mg/L.
Description	Concentration used at base of vertical plane source (see figure below from Sale *et al*., 2008b). 
Typical Values	0.0001 – 20,000 mg/L.
Source of Data	*Data Source 1. Site History or Process Information.* For example, the effective solubility of a constituent in a known DNAPL pool in the source could be used when modeling the source zone, or if the DNAPL in the pool was comprised of 50% Trichloroethene (TCE), a concentration of 550 mg/L (50% of TCE solubility of 1100 mg/L) could be used. Alternatively, one could use an estimate of the average historical concentration from the time the source started to the end of the loading period; sometimes a groundwater model with a source decay term (such as REMChlor (Falta et al., 2007)) can be used to estimate historical groundwater concentrations in the early period of a plume's life cycle. *Data Source 2. Highest Observed Concentration.* More commonly, good Data Source 1 information will not be available. In that case, we recommend using the highest observed concentration from a groundwater monitoring point in the modeled area (the two boxes) and a groundwater concentration contour map from the period with the highest observed concentrations from the monitoring network. This is typically the oldest concentration contour map available. While not perfect, this method is based on real data and represents observed loading concentrations in the modeled area. **This value is a key parameter that can be changed during the calibration process to increase or decrease the simulated mass discharge or concentration to better match field data** (see the beginning of this section).

How to Enter Data	Enter directly.

PARAMETER	MOLECULAR DIFFUSION COEFFICIENT IN FREE WATER (D_o)
Units	cm^2/sec, m^2/sec.
Description	A factor of proportionality representing the amount of substance diffusing across a unit area through a unit concentration gradient in unit time.
Typical Values	Benzene 9.8E-06 cm^2/s; Ethylbenzene 7.8E-06 cm^2/s; Toluene 8.6-06 cm^2/s; Xylene 8.5E-06 cm^2/s; MTBE 9.4E-05 cm^2/s; Tetrachloroethene 8.2E-06 cm^2/s; Trichloroethene 9.1E-06 cm^2/s; cis-1,2-Dichloroethene 1.1E-05 cm^2/s; Vinyl Chloride 1.2E-05 cm^2/s; 1,1,1-Trichloroethane 8.8E-06 cm^2/s (TRRP, 2008.) (Note that there is a wide range of reported values, for example, Wiedemeier *et al*. (1999) report a D_o for benzene of 1.1E-05 cm^2/s.) For more information, see Pankow and Cherry, 1996 (for solvents) and Wiedemeier *et al*., 1999 (variety of constituents).
Source of Data	Chemical reference literature such as Pankow and Cherry, 1996 (for solvents); Wiedemeier *et al*., 1999 (variety of constituents); or other references with chemical properties.
How to Enter Data	1) Select units, and 2) Enter directly. (Note that if the constituent is selected from the drop down list, the Toolkit provides a default value for the parameter.)

PARAMETER	TRANSMISSIVE ZONE APPARENT TORTUOSITY FACTOR EXPONENT (p)
Units	Unitless.
Description	The Apparent Tortuosity Factor (τ) relates the molecular diffusion coefficient in free water (D_o) of a constituent in a porous medium to its effective diffusion coefficient (D_e). Values of τ can range between 0 and 1. Estimations of τ can be obtained using the relationship: $$\frac{D_e}{D_o} = \tau \cong \emptyset^p$$ Where $\boldsymbol{\Phi}$ is the porosity and *p* the Apparent Tortuosity Factor Exponent. Depending on the geologic medium, values for *p* can vary between 0.3 and 5.4 (Charbeneau, 2000; Pankow and Cherry, 1996; Dullien, 1992; Lerman, 1979; and Millington and Quirk, 1961).
Typical Values	Sand: 0.33 Silt: 0.33 (Payne *et al*., 2008.)
Source of Data	Literature.
How to Enter Data	Enter directly. (Note that if the transmissive zone description is selected from the drop down list, the Toolkit provides a value for the parameter.)

PARAMETER	LOW-k ZONE APPARENT TORTUOSITY FACTOR EXPONENT (p′)
Units	Unitless.
Description	The Apparent Tortuosity Factor (τ) relates the molecular diffusion coefficient in free water (D_o or D_{aq}) of a constituent in a porous medium to its effective diffusion coefficient (D_e). Values of τ can range between 0 and 1. Estimations of τ can be obtained using the relationship: $$\frac{D_e}{D_o} = \tau \cong \emptyset^p$$ Where $\boldsymbol{\Phi}$ is the porosity and p the Apparent Tortuosity Factor Exponent. Depending on the geologic medium, values for *p* can vary between 0.3 and 5.4 (Charbeneau, 2000; Pankow and Cherry, 1996; Dullien, 1992; Lerman, 1979; and Millington and Quirk, 1961).
Typical Values	Clay: 1.33 Fractured Sandstone: 0.63 Granite: 0.57 Sandstone/Shale: 1 Silt: 0.33 (Payne *et al*., 2008.)
Source of Data	Literature.
How to Enter Data	Enter directly. (Note that if the low-k zone description is selected from the drop down list, the Toolkit provides a value for the parameter).

PARAMETER	BULK DENSITY OF TRANSMISSIVE ZONE (ρ_b)
Units	g/mL.
Description	Density of the saturated transmissive zone aquifer material (referred to as "soil"), excluding soil moisture.
Typical Values	Although this value can be measured in the lab, in most cases estimated values are used. A value of 1.7 g/mL is used frequently.
Source of Data	Either from an analysis of soil samples at a geotechnical lab or more commonly, application of estimated values such as 1.7 g/mL.
How to Enter Data	Enter directly.

PARAMETER	SOIL BULK DENSITY OF LOW-k ZONE (ρ'_b)
Units	g/mL.
Description	Density of the saturated low-k zone (referred to as "soil"), excluding soil moisture.
Typical Values	Although this value can be measured in the lab, estimated values are used in most cases. A value of 1.7 g/mL is used frequently for unconsolidated media. Representative values for specific geologic media are shown below (Lovanh *et al*., 2000; derived from Domenico and Schwartz, 1990): Clay: 1.0 - 2.4 — Loess: 0.75 - 1.6 Sandstone: 1.6 - 2.68 — Shale: 1.54 - 3.17 Limestone: 1.74 - 2.79 — Granite: 2.24 - 2.46 Basalt: 2 - 2.7 — Medium Sand: 1.34 - 1.81

	Koerner (1984) reports these values for unit weight for saturated soils (note no dry bulk density values are reported for these materials): Glacial till, very mixed grain: 2.32 — Soft glacial clay: 1.77 Stiff glacial clay: 2.07 — Soft slightly organic clay: 1.58 Soft very organic clay: 1.43 — Soft bentonite: 1.27
Source of Data	Either from an analysis of soil samples at a geotechnical lab or more commonly, application of estimated values such as 1.7 g/mL.
How to Enter Data	Enter directly.

PARAMETER	**TRANSMISSIVE ZONE FRACTION ORGANIC CARBON (f_{oc})**
Units	Unitless.
Description	Fraction of the aquifer material comprised of natural organic carbon in uncontaminated areas. More natural organic carbon means higher adsorption of organic constituents on the aquifer matrix.
Typical Values	0.0002 - 0.02 for transmissive zones.
Source of Data	The fraction organic carbon value should be measured, if possible, by collecting a sample of aquifer material from an uncontaminated saturated zone and performing a laboratory analysis for transmissive zones (e.g., ASTM Method 2974-87 or equivalent). If unknown, a default value of 0.001 is often used (e.g., ASTM 1995).
How to Enter Data	Enter directly.

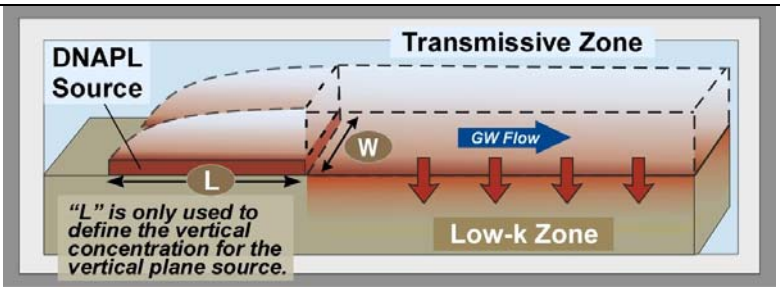
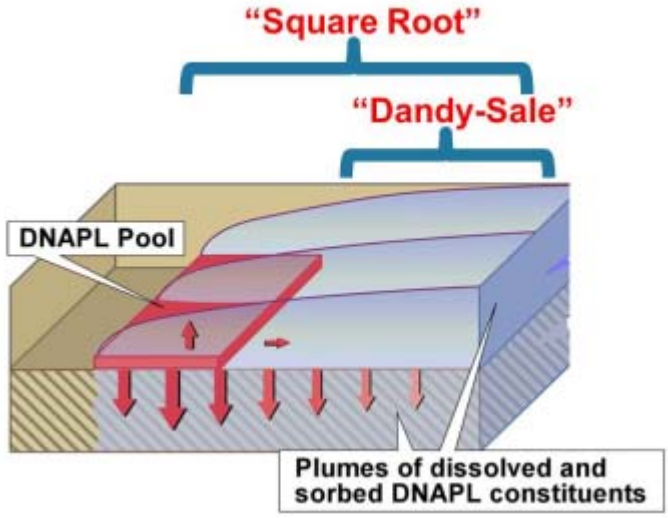
PARAMETER	**LOW-k ZONE FRACTION ORGANIC CARBON (f'_{oc})**
Units	Unitless (gram per gram).
Description	Fraction of the aquifer material comprised of natural organic carbon in uncontaminated areas. More natural organic carbon means higher adsorption of organic constituents on the aquifer matrix.
Typical Values	Although based on limited data, 0.0002 - 0.10 for low-K zones is a likely range. But, some sites may be higher or lower. Examples: At the Moffatt Field site, the f_{oc} of the clay fraction is about 0.0066 (Roberts *et al.*, 1990). Domenico and Schwartz (1990) report these values: silt (Wildwood Ontario): 0.00102; from Oconee River sediment: coarse silt: 0.029; medium silt: 0.02; fine silt: 0.0226. Chapman and Parker (2005) report a f_{oc} of glaciolacustrine aquitard composed of varved silts and clays: 0.0024 to 0.00104 with an average of 0.00054. Adamson (2012) reports f_{oc} = 0.001 for a clay layer in Jacksonville, Florida and f_{oc} values for silts at the MMR site in Massachusetts ranging from <0.0005 to 0.0022 (median value = 0.0014) for one core using Leco carbon analyzer; a second core had f_{oc} values < 0.005 for 10 samples and two samples with 0.00067 and 0.00084 (gram per gram). Values for f_{oc} using Walkley-Black wet oxidation method were generally higher by a factor of

	2 to 3. Values ranging from 0 to 0.078 have been reported for silts at the F.W. Warren site in Wyoming, with a median value of 0.
Source of Data	The fraction organic carbon value should be measured, if possible, by collecting a sample of aquifer material from an uncontaminated saturated zone and performing a laboratory analysis (e.g., ASTM Method 2974-87 or equivalent). If unknown, a default value of 0.002 should be used (twice the typical default of 0.001 value used for transmissive systems).
How to Enter Data	Enter directly.

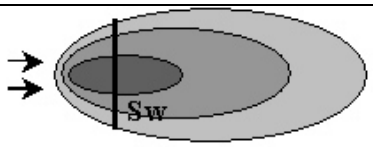
PARAMETER	**ORGANIC CARBON PARTITIONING COEFFICIENT (K_{oc})**
Units	mL/g
Description	Chemical-specific partition coefficient between soil organic carbon and the aqueous phase. Larger values indicate greater affinity of organic constituents for the organic carbon fraction of soil. This value is chemical specific and can be found in chemical reference books.
Typical Values	Tetrachloroethene 155 mL/g; Benzene 66 mL/g Trichloroethene 93 mL/g; Ethylbenzene 204 mL/g cis-1,2-Dichloroethene 29 mL/g; Toluene 140 mL/g Vinyl Chloride 11 mL/g; Xylene 240 mL/g 1,1,1-Trichloroethane 110 mL/g; MTBE 14 mL/g (TRRP, 2008.) (Note that there is a wide range of reported values, for example, Mercer and Cohen (1990) report a K_{oc} for benzene of 83 mL/g.) For more information, see Pankow and Cherry, 1996 (for solvents) and Wiedemeier *et al*., 1999 (variety of constituents).
Source of Data	Chemical reference literature such as Pankow and Cherry, 1996 (for solvents); Wiedemeier *et al*., 1999 (variety of constituents); or other references with chemical properties. Alternatively, one can use relationships between K_{oc} and solubility or K_{oc} and the octanol-water partition coefficient (K_{ow}) to determine K_{oc}. A collection of values is presented in the Chemical Parameter Database included in this manual.
How to Enter Data	Enter directly. (Note that if the constituent is selected from the drop down list, the Toolkit provides a value for the parameter.)

Step 4: *Source Zone Characteristics*

PARAMETER:	**SOURCE ZONE LENGTH (L)**
Units	ft (m).
Description	Estimated length of the original source zone parallel to groundwater flow that is upgradient of the modeled area. This length is only used to establish a parameter that exponentially reduces the vertical concentration in the vertical source plane (by the "W" in the figure below). Close to the bottom of the vertical plane source, the concentration is equal to C_o (page 42); at the top of the vertical plane the concentration is lower based on equation 3 on page 78 which uses α_t (page 48) which in turn is a function of L. You can ignore L and just enter your own value of α_t if you prefer.

	 This is conceptualized in Sale *et al*., (2008b) as a DNAPL pool upgradient of the modeled zone; the Dandy-Sale Model simulates matrix diffusion in the downgradient plume (see figure below). 
Typical Values	10 - 500 ft (3 - 152 m).
Source of Data	To determine source length across the site, draw a line parallel to the direction of groundwater flow in what is considered to be the high concentration source area. The DSM source length is not a highly sensitive parameter in the model; if unsure of which value to use, enter about 100 ft.
How to Enter Data	Enter directly.

PARAMETER:	**SOURCE ZONE WIDTH (W)**
Units	ft (m).
Description	The estimated width of the source zone perpendicular to the groundwater flow.
Typical Values	0 - 500 ft (0 - 152 m).
Source of Data	To determine source width across the site, draw a line perpendicular to the direction of groundwater flow in what is considered to be the high concentration source area.

	
How to Enter Data	Enter directly.

PARAMETER	SOURCE LOADING STARTS IN YEAR
Units	Year (yyyy).
Description	Year source loading started. Estimated from site historical records and is usually from the 1950s, 1960s, 1970s, or early1980s. If the release was over a long period of time, usually it is better to enter the earliest year.
How to Enter Data	Enter directly.

PARAMETER	SOURCE REMOVED IN YEAR
Units	Year (yyyy).
Description	Year source was removed. This is either: 1) the year that best represents when concentrations in the middle of the modeled area were reduced significantly by source remediation; or 2) when source zone natural attenuation processes reduced the concentrations in the middle of the modeled area significantly. For example, the source could likely be considered removed by natural attenuation for the purposes of this model if the transmissive zone of the modeled area have been reduced by 90% or 99% compared to the historical all-time concentrations.
How to Enter Data	Enter directly.

PARAMETER	TRANSVERSE (VERTICAL) HYDRODYNAMIC DISPERSIVITY (α_t)
Units	ft (m).
Description	Hydrodynamic dispersion is the macroscopic spreading of a dissolved constituent plume due to effects of chemical diffusion and mechanical dispersion. Mechanical dispersion is caused by the small-scale variations in flow velocity through porous media causing the paths of solutes to spread from the overall direction of groundwater flow. Transverse (vertical) hydrodynamic dispersivity defines how strong the mechanical mixing component is. For the Dandy-Sale model, this value is used to define the vertical distribution of concentration at the vertical plane source (see equation 3 of Appendix A.2.1) and spreads the plume out vertically as it progresses downstream. For the Toolkit, we assume that the transverse (vertical) hydrodynamic dispersivity is relatively small (no more than 0.001 meters) for two reasons: 1) there is a new, low dispersion paradigm emerging in the solute transport field; and 2) since the Toolkit is calculating concentration from a horizontal mass flux equation, we have to assume a plume never disperses more than 10 feet above the low-k/transmissive zone contact (we assume a 10-foot monitoring well is used to determine groundwater concentrations in the model).

Typical Values	For this model: $\alpha_t \leq 0.0004$ ft (0.001 m).
Source of Data	Typically estimated using empirical relationships.
How to Enter Data	Enter directly. The Toolkit automatically assigns a maximum value of 0.0004 ft (0.001 m). This value can be overwritten. Use the "Restore" button to restore the Toolkit calculated value.

Step 5: *General*

PARAMETER	SEE RELEASE PERIOD RESULTS FOR YEAR
Units	Year (yyyy).
Description	Year for displaying matrix diffusion results.
How to Enter Data	Enter directly.

PARAMETER	LATERAL DISTANCE FROM SOURCE (x)
Units	ft (m).
Description	Lateral distance from source for displaying matrix diffusion results. Note: Due to computational limitations, all transmissive zone solutions show increasing numerical imprecision for lengths greater than 4921 ft (1500 m). Therefore, we recommend limiting the lateral distance from the source to **≤ 4921 ft (1500 m)** for any model runs involving transmissive zone solutions (Appendix A.2.7 Equation 1).
How to Enter Data	Enter directly.

PARAMETER	DEPTH INTO LOW-K ZONE (z)
Units	ft (m).
Description	Vertical depth of the low-k zone from the source for displaying matrix diffusion results.
How to Enter Data	Enter directly.

PARAMETER	NEXT STEP: SHOW GRAPH
Description	Proceeds to the results of matrix diffusion analysis.

PARAMETER	SHOW PREVIOUS DATA
Description	Shows the output for previously run analysis.

PARAMETER	NEW SITE/CLEAR DATA

Description	Clears **ALL** data related to the DSM model in the Toolkit memory banks. Use this button to start a new project.

PARAMETER	**PASTE EXAMPLE**
Description	Clears **ALL** data related to the DSM model in the Toolkit memory banks and pastes an example dataset. The example dataset used in the Toolkit is obtained from Chapman and Parker (2005).

PARAMETER	**SAVE DATA**
Description	Saves all the DSM model data. **DO NOT ADD ANY EXTENSIONS TO FILE NAME WHEN SAVING**. ***Note that this option does not save any edits performed on the graphs by the user. To save such edits, use the save function of Excel® and save the entire Toolkit file.***

PARAMETER	**LOAD DATA**
Description	Loads data files saved through the Toolkit. **DO NOT EDIT ANY TOOLKIT FILES**. Editing files may cause the Toolkit to crash.

PARAMETER	**RETURN TO MODEL SELECTION SCREEN**
Description	Returns to the Model Selection Screen.

PARAMETER	**RETURN TO MAIN SCREEN**
Description	Returns to the Matrix Diffusion Toolkit Main Screen.

DSM Model Results

NOTE: Due to run-time constraints, the DSM does not automatically produce results over multiple times. The user can manually run the model for various times as necessary.

PARAMETER	SEE 2-D LOW-K AQUEOUS CONC
Description	Output showing the low-k zone aqueous concentrations along the lateral distance from the source as a function of depth in the low-k zone.

PARAMETER	SEE LOW-K AQ CONC VS. DIST
Description	Concentration vs. distance in the low-k zone. The user may use the *Log←→Linear* button to see the results on a semi-log plot.

PARAMETER	SEE LOW-K AQ CONC VS. DEPTH
Description	Concentration vs. depth in the low-k zone. The user can vary the lateral distance from source at which to view results by: 1. Entering the distance, and 2. Then pressing the "Update Graph" button. The user may use the *Log←→Linear* button to see the results on a semi-log plot.

PARAMETER	SEE 2-D LOW-K SORBED CONC
Description	Output showing the low-k zone sorbed concentrations along the lateral distance from the source as a function of depth in the low-k zone.

PARAMETER	SEE 2-D LOW-K TOTAL CONC
Description	Output showing the low-k zone total concentrations along the lateral distance from the source as a function of depth in the low-k zone.

PARAMETER	SEE TRANS. ZONE AQUEOUS CONC
Description	Aqueous phase concentration vs. distance in the transmissive zone. Concentration is calculated by assuming a 10-foot screened interval. The 10-foot screened interval was selected because at an actual field site, contamination diffusing from a low-k zone might spread vertically above a 1-foot screen. It was thought to be very unlikely that there would be more than 10 feet of vertical spreading in the transmissive zone. Bottom line: the 10-foot screened interval is hard-wired into the model and cannot be changed by the user. If you are sure all the mass discharge is being captured by a well with a

	different screened interval, you can get the simulated concentration in this well by multiplying the model output by the ratio of the screens (your screened interval ÷ 10 feet). The user may use the *Log←→Linear* button to see the results on a semi-log plot.

PARAMETER	SEE TRANS. ZONE MASS DISCHARGE
Description	Mass discharge vs. distance in the transmissive zone. The user may use the *Log←→Linear* button to see the results on a semi-log plot.

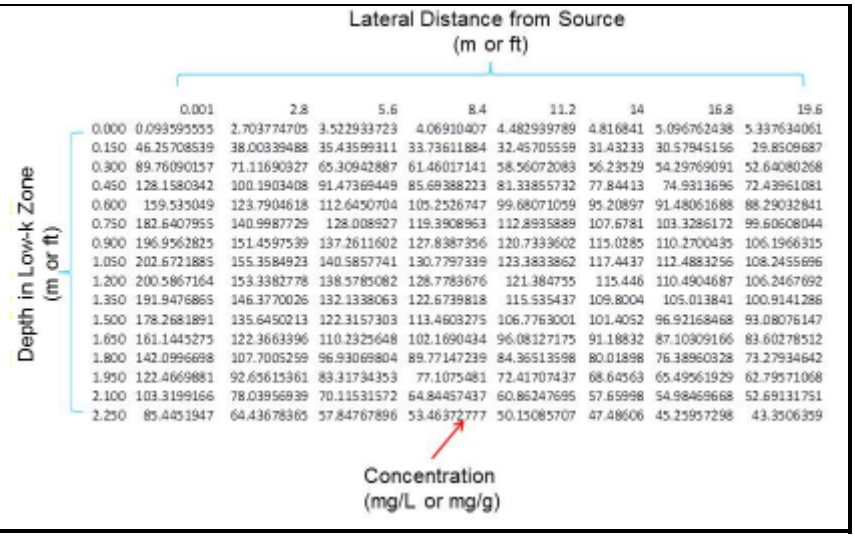
PARAMETER	SEE TRANS. ZONE SORBED CONC
Description	Sorbed phase concentration vs. distance in the transmissive zone. The user may use the *Log←→Linear* button to see the results on a semi-log plot.

PARAMETER	SEE TRANS. ZONE TOTAL CONC
Description	Total concentration vs. distance in the transmissive zone. The user may use the *Log←→Linear* button to see the results on a semi-log plot.

PARAMETER	MASS RESULTS
Description	The Toolkit also estimates the contaminant mass in both the low-k and transmissive zones. Mass is reported as aqueous phase, sorbed phase, and total (aqueous plus sorbed).

PARAMETER	NEXT STEP: SAVE DATA
Description	Saves all the DSM model data. **DO NOT ADD ANY EXTENSIONS TO FILE NAME WHEN SAVING**. ***Note that this option does not save any edits performed on the graphs by the user. To save such edits, use the save function of Excel® and save the entire Toolkit file.***

PARAMETER	EXPORT LOW-k 2-D DATA
Description	Exports the 2-D low-k aqueous, sorbed, and total concentration data into a text file for use in other programs. The exported file follows the format:

Depth in Low-k Zone (m or ft)	0.001	2.8	5.6	8.4	11.2	14	16.8	19.6
0.000	0.093595555	2.703774705	3.522933723	4.06910407	4.482939789	4.816841	5.096762438	5.337634061
0.150	46.25708539	38.00339488	35.43599311	33.73611884	32.45705559	31.43233	30.57945156	29.8509687
0.300	89.76090157	71.11690327	65.30942887	61.46017141	58.56072083	56.23529	54.29769091	52.64080268
0.450	128.1580342	100.1903408	91.47369449	85.69388223	81.33855732	77.84413	74.9313696	72.43961081
0.600	159.535049	123.7904618	112.6450704	105.2526747	99.68071059	95.20897	91.48061688	88.29032841
0.750	182.6407955	140.9987729	128.008927	119.3908963	112.8935889	107.6781	103.3286172	99.60608044
0.900	196.9562825	151.4597539	137.2611602	127.8387356	120.7333602	115.0285	110.2700435	106.1966315
1.050	202.6721885	155.3584923	140.5857741	130.7797339	123.3833862	117.4437	112.4883256	108.2455696
1.200	200.5867164	153.3382778	138.5785082	128.7783676	121.384755	115.446	110.4904687	106.2467692
1.350	191.9476865	146.3770026	132.1338063	122.6739818	115.535437	109.8004	105.013841	100.9141286
1.500	178.2681891	135.6450213	122.3157303	113.4603275	106.7763001	101.4052	96.92168468	93.08076147
1.650	161.1445275	122.3663396	110.2325648	102.1690434	96.08127175	91.18832	87.10909166	83.60278512
1.800	142.0996698	107.7005259	96.93069804	89.77147239	84.36513598	80.01898	76.38960328	73.27934642
1.950	122.4669881	92.63615361	83.31734353	77.1075481	72.41707437	68.64563	65.49561929	62.79571068
2.100	103.3199166	78.03956839	70.11531572	64.84457437	60.86247695	57.65998	54.98469668	52.69131751
2.250	85.4451947	64.43678365	57.84767896	53.46372777	50.15085707	47.48606	45.25957298	43.3506359

PARAMETER	RETURN TO DSM DATA INPUT
Description	Returns to the DSM data input screen.

PARAMETER	RETURN TO MAIN SCREEN
Description	Returns to the Toolkit Main Screen.

NAPL DISSOLUTION MODEL DATA ENTRY

Three important considerations regarding data input are:

1) To see the example dataset in the input screen of the software, click on the *Paste Example* button on the lower right portion of the input screen.

2) Because the Toolkit is based on an Excel® spreadsheet, you have to click outside of the cell where you just entered data or hit *Return* before any of the buttons will function. Additionally, **REMOVING OR ADDING** rows or columns in input screens may cause the program to crash.

3) Parameters used in the model are to be entered directly into the white/blue cells.

NOTE: Although literature values are provided, site-specific hydrogeologic, transport, and plume characteristic values will likely provide better results. If literature values are used and there is uncertainty in the value chosen, sensitivity analyses should be conducted to determine the effects of the uncertainty on model predictions.

NAPL Dissolution Model Data Input Screen:

This module calculates the dissolution rate from the top of a DNAPL pool (bottom of a LNAPL pool), but not through the NAPL pool therefore, the dissolution rate is likely underestimated.

Step 1: *System Units*

PARAMETER	SYSTEM UNITS
Description	Unit system to perform calculations in.
Units	SI System (meters, etc.) or English Units (feet, etc.).
How to Enter Data	Choose the appropriate radio button.

Step 2: *Hydrogeology – Transmissive Zone*

PARAMETER	UNIT DESCRIPTION
Description	Description of the transmissive zone.
How to Enter Data	Choose from drop down list or enter directly.

PARAMETER	POROSITY (ϕ)
Units	Unitless.
Description	Dimensionless ratio of the volume of voids to the bulk volume of the surface soil column matrix. Note that *total porosity* is the ratio of all voids (including non-connected voids) to the bulk volume of the aquifer matrix. Differences between total and effective porosity reflect lithologic controls on pore structure. In unconsolidated sediments coarser than silt size, effective porosity can be less than total porosity by 2-5% (e.g., 0.28 vs. 0.30) (Smith and Wheatcraft, 1993). For this implementation of the model, effective porosity is typically used and is assumed to be similar to total porosity for mass and mass transfer calculations. (In other words, to simplify the model, both effective and total porosity are not entered separately, but assumed to be the same value).
Typical Values	Values for effective porosity: Silt 0.01 - 0.30 Gravel 0.10 - 0.35 Fine Sand 0.10 - 0.30 Medium Sand 0.15 - 0.30 Coarse Sand 0.20 - 0.35 (From Wiedemeier *et al*., 1999; originally from Domenico and Schwartz, 1990 and Walton, 1988).
Source of Data	Typically estimated. Occasionally obtained through physical property testing of site soil samples. One commonly used value for silts and sands is an effective porosity of 0.25. The ASTM RBCA Standard (ASTM, 1995) includes a default value of 0.38 (to be used primarily for unconsolidated deposits). A collection of default values is presented in the Geologic Parameter Database included in this manual.
How to Enter Data	Enter directly. (Note that if the transmissive zone description is selected from the drop down list, the Toolkit provides a default value for the parameter.)

PARAMETER	SEEPAGE VELOCITY (V)
Units	cm/sec, ft(or m)/day, ft(or m)/yr.
Description	Actual interstitial groundwater velocity, equaling Darcy velocity divided by effective porosity.
Typical Values	1 - 1500 ft/yr (0.3 - 457 m/yr).
Source of Data	Calculated by multiplying hydraulic conductivity by hydraulic gradient and dividing by effective porosity ($V = (K \times i) / n_e$). It is strongly recommended that actual site data be used for hydraulic conductivity and hydraulic gradient data parameters; effective porosity can be estimated.
How to Enter Data	1) Select units and enter directly, or 2) Calculate entering values for: a) Hydraulic conductivity, b) Hydraulic gradient, and c) Pressing the "Calculate V" button.

PARAMETER	HYDRAULIC CONDUCTIVITY (K)
Units	cm/sec, ft(or m)/day, ft(or m)/yr.
Description	Measure of the permeability of the transmissive layer. To characterize concentrations in the transmissive layer, representative measurements are required for the Darcy velocity (or both the hydraulic flow gradient and the hydraulic conductivity) of the flow system. Representative measurements of hydraulic conductivity of the transmissive layer should be obtained at one or more locations using appropriate slug test or pumping test methods (Newell *et al*., 2003).
Typical Values	Silts: $1x10^{-6}$ - $1x10^{-3}$ cm/s Silty sands: $1x10^{-5}$ - $1x10^{-1}$ cm/s Clean sands: $1x10^{-3}$ - 1 cm/s Gravels: > 1 cm/s (Newell *et al*., 1996.)
Source of Data	Pump tests or slug tests at the site. It is strongly recommended that actual site data be used for all matrix diffusion evaluations.
How to Enter Data	1) Select units, and 2) Enter directly.

PARAMETER	HYDRAULIC GRADIENT (i)
Units	ft/ft (or m/m).
Description	The slope of the potentiometric surface. In unconfined aquifers, this is equivalent to the slope of the water table.
Typical Values	0.0001 - 0.1 ft/ft (0.0001 - 0.1 m/m).
Source of Data	Calculated by constructing potentiometric surface maps using static water level data from monitoring wells and estimating the slope of the potentiometric surface.

How to Enter Data	Enter directly.

Step 3: *Transport*

PARAMETER	KEY CONSTITUENT
Description	Constituent of interest.
How to Enter Data	Enter directly or choose from drop down list.

PARAMETER	VERTICAL TRANSVERSE DISPERSIVITY (α_v)
Units	ft (m).
Description	Dispersion refers to the process whereby a dissolved solvent will be spatially distributed because of mechanical mixing and chemical diffusion in the aquifer. These processes develop the "plume" shape that is the spatial distribution of the dissolved solvent mass in the aquifer. Selection of dispersivity values is a difficult process given the impracticability of measuring dispersion in the field. However, simple estimation techniques based on the length of the plume or distance to the measurement point ("scale") are available from a compilation of field test data.
Typical Values	0.05 times the modeled length (Aziz *et al*., 2000), in this case the NAPL pool length.
Source of Data	Typically estimated using empirical relationships.
How to Enter Data	Enter directly.

PARAMETER	MOLECULAR DIFFUSION COEFFICIENT IN FREE WATER (D_o)
Units	cm^2/sec, m^2/sec.
Description	A factor of proportionality representing the amount of substance diffusing across a unit area through a unit concentration gradient in unit time.
Typical Values	Benzene 9.8E-06 cm^2/s; Ethylbenzene 7.8E-06 cm^2/s; Toluene 8.6-06 cm^2/s; Xylene 8.5E-06 cm^2/s; MTBE 9.4E-05 cm^2/s; Tetrachloroethene 8.2E-06 cm^2/s; Trichloroethene 9.1E-06 cm^2/s; cis-1,2-Dichloroethene 1.1E-05 cm^2/s; Vinyl Chloride 1.2E-05 cm^2/s; 1,1,1-Trichloroethane 8.8E-06 cm^2/s (TRRP, 2008) (Note that there is a wide range of reported values; for example, Wiedemeier *et al*. (1999) report a D_o for benzene of 1.1E-05 cm^2/s.) For more information, see Pankow and Cherry, 1996 (for solvents) and Wiedemeier *et al*., 1999 (variety of constituents).
Source of Data	Chemical reference literature such as Pankow and Cherry, 1996 (for solvents); Wiedemeier *et al*., 1999 (variety of constituents); or other references with chemical properties.
How to Enter Data	1) Select units, and 2) Enter directly. (Note that if the constituent is selected from the drop down list, the Toolkit provides a default value for the parameter.)

PARAMETER	APPARENT TORTUOSITY FACTOR EXPONENT (p)
Units	Unitless.
Description	The Apparent Tortuosity Factor (τ) relates the molecular diffusion coefficient in free water (D_o) of a constituent in a porous medium to its effective diffusion coefficient (D_e). Values of τ can range between 0 and 1. Estimations of τ can be obtained using relationship: $$\frac{D_e}{D_o} = \tau \cong \emptyset^p$$ Where ***Φ*** is the porosity and *p* the Apparent Tortuosity Factor Exponent. Depending on the geologic medium, values for *p* can vary between 0.3 and 5.4 (Charbeneau, 2000; Pankow and Cherry, 1997; Dullien, 1992; Lerman, 1979; and Millington and Quirk, 1961).
Typical Values	Sand: 0.33 Silt: 0.33 (Payne *et al.*, 2008.)
Source of Data	Literature.
How to Enter Data	Enter directly. (Note that if the transmissive zone description is selected from the drop down list, the Toolkit provides a default value for the parameter.)

Step 4: *Plume Characteristics*

PARAMETER	SOLUBILITY OF KEY CONSTITUENT (C_S)
Units	ug/L or mg/L.
Description	Solubility of key NAPL constituent.
Typical Values	0.0001 - 1100 mg/L.
Source of Data	Literature.
How to Enter Data	Enter directly. (Note that if the constituent is selected from the drop down list, the Toolkit provides a default value for the parameter.)

PARAMETER:	LENGTH OF NAPL POOL (L)
Units	ft (m).
Description	Estimated length of the NAPL area to be modeled.
Typical Values	10 - 500 ft (3 - 152 m).
How to Enter Data	Enter directly.

PARAMETER:	HEIGHT OF NAPL POOL (H)
Units	ft (m).
Description	Estimated height of the NAPL area to be modeled.
Typical Values	0 - 5 ft (0 - 1.2 m).
Source of Data	Monitoring well data.
How to Enter Data	Enter directly.

PARAMETER:	WIDTH OF NAPL POOL (W)
Units	ft (m).
Description	Estimated width of the NAPL area to be modeled.
Typical Values	10 - 500 ft (3 - 152 m).
Source of Data	Monitoring well data.
How to Enter Data	Enter directly.

PARAMETER	NAPL DENSITY (ρ_{NAPL})
Units	g/cm^3.
Description	Density of the NAPL.

Typical Values	0.80 - 1.4.
Source of Data	From an analysis of representative NAPL samples or from literature values.
How to Enter Data	Enter directly.

PARAMETER	**NAPL SATURATION (S_o)**
Units	Unitless.
Description	An estimate of the fraction of the pore space filled with NAPL.
Typical Values	0 - 0.30. For a discussion of NAPL saturation at solvent sites, see Pankow and Cherry, 1996. For a detailed discussion of solvents and fuels, see Mercer and Cohen, 1990. For a brief summary, see Chapter 2 of Wiedemeier *et al*., 1999.
Source of Data	This value can be measured by analyzing soil samples. Without site-specific measurements, the uncertainty in the estimates will likely be an order-of-magnitude or greater.
How to Enter Data	Enter directly.

NAPL Dissolution Model Results

PARAMETER	MASS FLUX DUE TO DIFFUSION FROM TOP OF NAPL POOL
Description	Mass flux due to diffusion from the top of the NAPL pool.

PARAMETER	NUMBER OF YEARS FOR DISSOLUTION OF NAPL PLUME
Description	The time required for the dissolution of the NAPL plume.

PARAMETER	NEXT STEP: SAVE DATA
Description	Saves all the NAPL Dissolution model data. **DO NOT ADD ANY EXTENSIONS TO FILE NAME WHEN SAVING**.

PARAMETER	NEW SITE/CLEAR DATA
Description	Clears **ALL** data related to the NAPL Dissolution model in the Toolkit memory banks. Use this button to start a new project.

PARAMETER	PASTE EXAMPLE
Description	Clears ALL data related to the NAPL Dissolution model in the Toolkit memory banks and pastes an example dataset.

PARAMETER	LOAD DATA
Description	Loads data files saved through the Toolkit. **DO NOT EDIT ANY TOOLKIT FILES**. Editing files may cause the Toolkit to crash.

PARAMETER	RETURN TO MODEL SELECTION SCREEN
Description	Returns to the Model Selection Screen.

PARAMETER	RETURN TO MAIN SCREEN
Description	Returns to the Matrix Diffusion Toolkit Main Screen.

CHEMICAL PARAMETER DATABASE

Chemical Name	Organic Carbon Petitioning Coefficient (log (Koc) @20-25 °C)) (log (1/kg))*	Solubility (@20-25 °C) (mg/L)*
Acetone	-0.24	1.00×10^{6}
Acenaphthene	3.85	3.93×10^{0}
Acenaphthylene	4.00	3.93×10^{0}
Anthracene	4.15	4.50×10^{-2}
Benzene	1.58	1.75×10^{3}
Benzoic acid	1.83	6.22×10^{4}
Benzo (a) Anthracene	6.14	5.70×10^{-3}
Benzo (b) Fluoranthane	5.74	1.47×10^{-2}
Benzo (k) Fluoranthene	5.74	4.30×10^{-3}
Benzo (g,h,i) Perylene	6.20	7.00×10^{-4}
Benzo (a) Pyrene	5.59	1.20×10^{-3}
Bromodichloromethane	1.85	6.22×10^{1}
Butanol, n-	0.74	7.70×10^{4}
Carbon disulfide	2.47	2.30×10^{3}
Carbon tetrachloride	2.67	7.62×10^{2}
Chlorobenzene	2.46	4.45×10^{2}
Chloroethane	1.25	2.00×10^{4}
Chloroform	1.93	9.64×10^{3}
Chloromethane	1.40	4.00×10^{-3}
Chlorophenol, 2-	2.11	2.85×10^{4}
Chrysene	5.30	1.80×10^{-3}
Dibenzo (a,h) Anthracene	5.87	5.00×10^{-4}
Dibromochloromethane	2.05	5.25×10^{3}
Dichlorobenzene, (1,2) (-o)	3.32	1.50×10^{2}
Dichlorobenzene, (1,4) (-p)	3.33	1.45×10^{2}
Dichlorodifluoromethane	2.12	1.98×10^{3}
Dichloroethane, 1,1-	1.76	5.00×10^{3}
Dichloroethane, 1,2-	1.76	8.69×10^{3}
Dichloroethene, cis1,2-	1.38	8.00×10^{2}

Chemical Name	Organic Carbon Petitioning Coefficient (log (Koc) @20-25 °C)) (log (1/kg))*	Solubility (@20-25 °C) (mg/L)*
Dichloroethene, trans1,2-	1.46	1.75×10^{3}
Ethylbenzene	1.98	6.00×10^{2}
Ethylene glycol	-0.90	1.00×10^{6}
Fluoranthene	4.58	2.06×10^{-1}
Fluorene	3.86	1.69×10^{0}
Hexane, n-	2.68	1.30×10^{1}
Indeno (1,2,3,c,d) Pyrene	7.53	7.17×10^{2}
Methanol	-0.69	1.00×10^{6}
Methylene chloride	1.23	1.54×10^{4}
Methyl ethyl ketone	0.28	2.18×10^{5}
Methyl t-Butyl Ether	1.08	4.80×10^{4}
Naphthalene	3.11	3.29×10^{1}
Phenanthrene	4.15	1.60×10^{0}
Phenol	1.44	9.30×10^{4}
Pyrene	4.58	1.60×10^{-1}
Tetrachloroethane 1,1,2,2-	0.00	7.18×10^{2}
Tetrachloroethene	2.43	1.43×10^{2}
Toluene	2.13	5.15×10^{2}
Trichlorobenzene	3.91	3.03×10^{1}
Trichloroethane 1,1,1-	2.45	1.26×10^{3}
Trichloroethane 1,1,2-	1.75	5.93×10^{3}
Trichloroethene	1.26	1.00×10^{3}
Trichlorofluoromethane	2.49	2.47×10^{3}
Vinyl Chloride	0.39	2.54×10^{3}
Xylene (mixed isomers)	2.38	1.98×10^{2}
Xylene, m-	3.20	1.58×10^{2}
Xylene, o-	2.11	1.75×10^{2}

* Values obtained from “Natural Attenuation of Fuels and Chlorinated Solvents in the Subsurface” by Wiedemeier *et al.*, 1999, Appendix B.

GEOLOGIC PARAMETER DATABASE

Parameter	Value	Units
Hydraulic Conductivity[1]		
Clean sands	0.001 - 1	cm/s
Clays	$<1 \times 10^{-6}$	cm/s
Gravels	>1	cm/s
Silts	1×10^{-6} - 1×10^{-3}	cm/s
Silty sands	1×10^{-5} - 1×10^{-1}	cm/s
Total Porosity[2]		
Basalt	0.03 - 0.35	(-)
Clay	0.34 - 0.60	(-)
Coarse Gravel	0.24 - 0.36	(-)
Fine Gravel	0.25 - 0.38	(-)
Fine Sand	0.26 - 0.53	(-)
Coarse Sand	0.31 - 0.46	(-)
Limestone	0.0 - 0.5	(-)
Sandstone	0.05 - 0.30	(-)
Shale	0.0 - 0.10	(-)
Silt	0.34 - 0.61	(-)
Siltstone	0.21 - 0.41	(-)
Effective Porosity[3]		
Clay	0.01 - 0.20	(-)
Fine Gravel	0.2 - 0.35	(-)
Medium Gravel	0.15 - 0.25	(-)
Coarse Gravel	0.1 - 0.25	(-)
Sandy Clay	0.03 - 0.2	(-)
Loess	0.15 - 0.35	(-)
Peat	0.3 - 0.5	(-)
Silt	0.01 - 0.3	(-)
Gravely Sand	0.2 - 0.35	(-)
Fine Sand	0.10 - 0.30	(-)
Medium Sand	0.15 - 0.30	(-)
Coarse Sand	0.20 - 0.35	(-)

Parameter	Value	Units
Effective Porosity[3]		
Glacial Sediments	0.05 - 0.2	(-)
Limestone	0.01 - 0.24	(-)
Unfractured Limestone	0.001 - 0.05	(-)
Sandstone	0.1 - 0.4	(-)
Siltstone	0.01 - 0.35	(-)
Fractured Granite	0.00005 - 0.01	(-)
Volcanic Tuff	0.02 - 0.35	(-)
Dry Bulk Density[2]		
Clay	1.00 - 2.40	(g/cm^3)
Silt	-	(g/cm^3)
Granite	2.24 - 2.46	(g/cm^3)
Fine Sand	1.37 - 1.81	(g/cm^3)
Medium Sand	1.37 - 1.81	(g/cm^3)
Coarse Sand	1.37 - 1.81	(g/cm^3)
Sandstone	1.60 - 2.68	(g/cm^3)
Gravel	1.36 - 2.19	(g/cm^3)
Limestone	1.74 - 2.79	(g/cm^3)

Notes:

1. From Newell *et al*., 1996.
2. From Wiedemeier *et al*., 1995.
3. From Wiedemeier *et al*., 1999 (originally from Domenico and Schwartz, 1990 and Walton, 1988).

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MATRIX DIFFUSION TOOLKIT TROUBLESHOOTING TIPS

Minimum System Requirements

The Matrix Diffusion Toolkit model requires a computer system capable of running Microsoft© Excel® (2007 or 2010) for Windows. Operation requires an IBM-compatible PC equipped with a Pentium or later processor running at a minimum of 450 MHz. A minimum of 256 MB of system memory (RAM) is strongly recommended. Computers not meeting these recommendations will experience slow running times and/or problems with memory.

Installation and Start-Up

The software is installed by unzipping the Toolkit model file (MatrixDiffusionToolkit.zip) and keeping all the unzipped files in the same folder on your computer hard drive. To use the software, start Excel® and load the MatrixDiffusionToolkit.xlsm model file from the File / Open menu. If you are using Excel® 2010, you may see a message box that asks you whether you want to disable or enable the macros. For the Toolkit to operate effectively, you must *enable* the macros.

NOTE: Although the Toolkit uses Microsoft© Excel®, some information in the 'Apply Related Tools' module calls Adobe© Acrobat® pdf documents. Some features in the module may not work unless you have this program installed on your computer.

Spreadsheet-Related Problems

Backspace doesn't clear cell. Use the delete key on the keyboard or the mouse to clear data.

The buttons won't work. The Toolkit is built in the Excel® spreadsheet environment, and to enter data one must click anywhere outside the cell where data was just entered. If you can see the numbers you just entered in the data entry part of Excel® above the spreadsheet, the data have not yet been entered. Click on another cell to enter the data.

is displayed in a number box. The cell format is not compatible with the value (e.g., the number is too big to fit into the window). To fix this, select the cell, pull down the format menu, select *Format Cells* and click on the *Number* tab. Change the format of the cell until the value is visible. If the values still cannot be read, select the format menu, select *Cells,* and click on the *Font* tab. Reduce the font size until the value can be read.

***#DIV/0!* is displayed in a number box.** The most common cause of this problem is that some input data are missing. In some cases, entering a zero in a box will cause this problem. Double check to make certain that data required for your run have been entered in all of the input cells.

***#VALUE!* is displayed in a number box.** The most common cause of this problem is that some input data are missing. Double check to make certain that data required for your run have been entered in all of the input cells and all options have been selected.

Common Error Messages

Unable to Load Help File: The most common error message encountered with the Toolkit is the message 'Unable to Open Help File' after clicking on a *Help* button. Depending on the version of Windows® you are using, you may get an Excel® Dialog Box, a Windows® Dialog Box, or you may

see Windows® Help load and display the error. This problem is related to the ease with which the Windows® Help Engine can find the data file, MatrixDiffusionToolkit.chm. Here are some suggestions (in decreasing order of preference) for helping WinHelp find it:

- If you are asked to find the requested file, do so. The file is called MatrixDiffusionToolkit.chm, and it was installed in the same directory/folder as the Matrix Diffusion Toolkit model file (MatrixDiffusionToolkit.xlsm).

- Use the File/Open menus from within Excel® instead of double-clicking on the filename or Program Manager icon to open the Matrix Diffusion Toolkit model file. This sets the *current directory* to the directory containing the Excel® file you just opened.

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Matrix Diffusion Toolkit Example Dataset:	The example dataset used in the Toolkit's SRM and DSM was obtained from Chapman and Parker (2005).

APPENDICES

APPENDIX A.1. SQUARE ROOT MODEL

Appendix A.1.1. Estimation of Mass Discharge

Purpose:
Determine the mass discharge output of the Square Root Model of the Matrix Diffusion Toolkit. Note: This derivation was originally developed by Parker *et al*.,1994 and is detailed in AFCEE, 2007.

Given:
There is a finite amount of soluble organic constituents in the source zone (in the dissolved, sorbed, and NAPL phases).

Assumptions:
The Toolkit uses a simplified conceptual model of a two-layer aquifer system (a transmissive layer and a low-k layer) where there are two different time periods:

1. A **loading period** where there is a constant concentration of contaminants in the transmissive zone that drives contaminants into the low-k zone.
2. A **release period**, where the transmissive zone is assumed to have no concentration, and an upper-range estimate of release from the low-k zone is generated.
3. The low-k zone is at least **1 meter thick**.
4. There is no degradation in the low-k zone.

Summary:
At any time t, transverse diffusion of contaminants into the low-k layer underlying the pool can be estimated using the equation:

$$M_d(t,t') = \phi C_s A\left(\sqrt{\frac{RD_e}{\pi t}} - \sqrt{\frac{RD_e}{\pi(t-t')}}\right)$$

Where:

M_d = Mass discharge (M/T);
t = Time since source was introduced (T);
t' = Time at which source was removed from the high-permeability compartment (T);
Φ = Porosity of low-k zone (unitless);
C_s = Mean plume concentration above the low-k compartment during the loading period (M/L^3);
A = Area of low-k compartment beneath the transmissive zone plume (L);
R = Retardation factor for low-k compartment (unitless); and
D_e = Effective aqueous phase diffusion coefficient in the low-k compartment (L2/T). This can be estimated as:

$$D_e = \phi^p D_o$$

where p is the apparent tortuosity factor exponent (unitless) and D_o the molecular diffusion coefficient in free water (L^2/T).

Appendix A.1.2. Estimation of Concentration in Transmissive Zone

Purpose:
Determine the transmissive zone concentration output of the Square Root Model of the Matrix Diffusion Toolkit.

Given:
The Toolkit provides an instantaneous mass discharge from the entire area "A" during the release period. Note this mass discharge from the entire low-k zone is assumed to be transported instantaneously to the downgradient edge of the modeled area (there is no advection or travel time component of the Square Root Model). But because diffusion from a low-k zone is typically much slower than the travel time in the transmissive zone (multiple decades vs. months or years), this approximation should not cause too much problem for most simulations. If travel time is an important part of the simulation, try using the DSM model.

Assumptions:
The Toolkit uses a simplified conceptual model of a two-layer aquifer system (a transmissive layer and a low-k layer) where there are two different time periods:

1. A **loading period** where there is a constant concentration of contaminants in the transmissive zone that drives contaminants into the low-k zone.
2. A **release period**, where the transmissive zone is assumed to have no concentration, and an upper-range estimate of release from the low-k zone is generated.
3. The low-k zone is at least **1 meter thick**.
4. There is no degradation in the low-k zone.
5. Mass discharge is occurring at a well with a 10-ft screened interval.

Summary:
At any time t, the concentration of contaminants in a transmissive zone can be estimated using the equation:

$$C(t) = \frac{M_d}{V_d H W}$$

Where:
$C(t)$ = Plume concentration in the transmissive zone at time t (M/L^3);
M_d = Mass discharge from the low-k layer into the transmissive layer (L/T);
V_d = Darcy velocity of the transmissive compartment (L/T);
H = Screened interval of the hypothetical well (L); and
W = Width of the modeled area (L).

Appendix A.1.3. Estimation of Mass in Transmissive Zone

Purpose:
Estimate the transmissive zone mass output of the Square Root Model of the Matrix Diffusion Toolkit.

Given:
There is a finite amount of soluble organic constituents in the source zone (in the dissolved, sorbed, and NAPL phases).

Assumptions:
The Toolkit uses a simplified conceptual model of a two-layer aquifer system (a transmissive layer and a low-k layer) where there are two different time periods:

1. A **loading period** where there is a constant concentration of contaminants in the transmissive zone that drives contaminants into the low-k zone.
2. A **release period**, where the transmissive zone is assumed to have no concentration, and an upper-range estimate of release from the low-k zone is generated.
3. The low-k zone is at least **1 meter thick**.
4. There is no degradation in the low-k zone.

Summary:
At any time t, mass discharge into the low-k layer underlying the pool can be estimated using the equation:

$$M_d(t,t') = \phi C_s A\left(\sqrt{\frac{RD_e}{\pi t}} - \sqrt{\frac{RD_e}{\pi(t-t')}}\right)$$

Where:

M_d = Mass discharge (M/T);
t = Time since source was introduced (T);
t' = Time at which source was removed from the high-permeability compartment (T);
Φ = Porosity of low-k zone (unitless);
C_s = Mean plume concentration above the low-k compartment (M/L^3);
A = Area of silt compartment beneath the plume (L^2);
R = Retardation factor for low-k compartment (unitless); and
D_e = Effective aqueous phase diffusion coefficient in the low-k compartment (L^2/T). This can be estimated as:

$$D_e = \phi^p D_o$$

where, p is the apparent tortuosity factor exponent (unitless) and D_o the molecular diffusion coefficient in free water (L^2/T).

Integrating this equation for mass yields (Seyedabbasi *et al*., 2012):

$$M(t,t') = 2\phi C_s \sqrt{\frac{RD_e}{\pi}} \left(\sqrt{t} - \sqrt{t - t'} \right)$$

APPENDIX A.2. DANDY-SALE MODEL

Appendix A.2.1. Low-k Aqueous Concentration

Purpose:
Determine the low-k aqueous concentration output in the Dandy-Sale Model of the Matrix Diffusion Toolkit. Note: This derivation was originally developed by Sale *et al*. 2008b and described in detail in Sale *et al.* (2008b) and Bolhari, 2012.

Given:
There is source material in a transmissive zone that loads up a downgradient low-k zone during the loading period before the source is removed.

Assumptions:
The Toolkit uses a simplified conceptual model of a two-layer aquifer system, a transmissive layer above a low-k layer (Figure A.2.1.1). A source (e.g., DNAPL) is introduced at the contact between the two layers. As shown in the figure, x is in the direction of groundwater flow, and z the direction perpendicular to groundwater flow. The edge of the source, at the interface between the two layers, is designated x=0 and z=0, with both x and z increasing with distance away from the source edge. In this model, z' is designated as the vertical depth from the source in the low-k layer, and z the height in the transmissive zone.

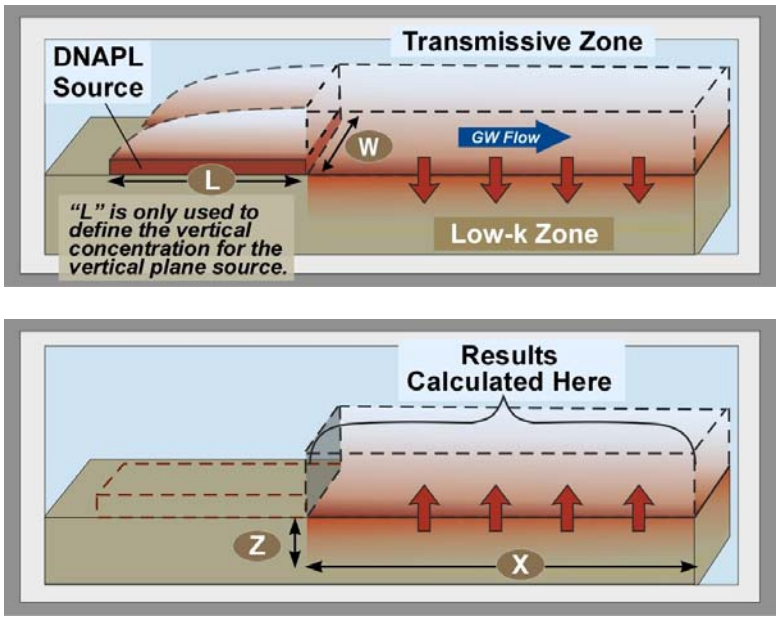

Figure A.2.1.1. The two-layer scenario conceptual model:
Top) Active Source, Bottom) Depleted Source

The model makes the following assumptions:

1. A *vertical* plane source at X=0 is assumed. This vertical plane has concentrations that decrease exponentially in the vertical direction the farther

one gets from the bottom of the transmissive zone. This exponential pattern is defined using the length of the source materials (L) upgradient of the vertical plane source and other factors using Equation 3 (it assumes vertical dispersion accounts for the vertical pattern).

2. A **loading period** occurs where there is a constant concentration of contaminants in the transmissive zone that drives contaminants into the low-k zone.
3. A **release period** occurs, where the transmissive zone is assumed to have no concentration, and an upper-range estimate of release from the low-k zone is generated.
4. There is no degradation in either layer.
5. Both layers are uniform, homogeneous, isotropic, and infinite in the z direction (perpendicular to groundwater flow).
6. One-dimensional (1-D) advective transport in the transmissive layer, parallel to the boundary of the layers, is accompanied by transverse dispersion and diffusion.
7. There is no longitudinal dispersion in the transmissive layer.
8. 1-D transverse diffusion transport occurs in the low-k layer.
9. Retardation of contaminants in both layers is based on instantaneous equilibrium between aqueous and sorbed phases.

Summary:

Active Source

While the source is active, the low-k aqueous concentration can be calculated at any time *t* using (Sale *et al*., 2008b):

$$C'(x,z',t) = C_o\left[\frac{1}{\sqrt{\pi}}\int_0^x \frac{I_1(x,z',t,\xi)}{\sqrt{x-\xi}}\left(\frac{1}{\sqrt{\pi\xi}} - \frac{b}{\varphi}e^{\frac{b^2\xi}{\varphi^2}}\operatorname{erfc}\left(\frac{b}{\varphi}\sqrt{\xi}\right)\right)d\xi\right] \qquad (1)$$

with $I_1(x,z',t,\xi)$, b, φ, D_t, D^*, V_c, R, R', and γ defined as:

$$I_1(x,z',t,\xi) = \operatorname{erfc}\left(\frac{\frac{z'}{\sqrt{\frac{D^*}{R'}}}}{2\sqrt{t-\frac{x}{V_c}}}\right) - \gamma\frac{\operatorname{erfc}\left(\frac{\frac{\gamma z'}{\sqrt{\frac{D^*}{R'}}}}{2\left(t-\frac{x}{V_c}\right)\sqrt{\frac{\gamma^2}{t-\frac{x}{V_c}}+\frac{\varphi^2}{x-\xi}}}\right)}{\sqrt{t-\frac{x}{V_c}}\sqrt{\frac{\gamma^2}{t-\frac{x}{V_c}}+\frac{\varphi^2}{x-\xi}}\exp\left(\frac{\frac{\varphi^2 z'^2}{\left(\frac{D^*}{R'}\right)}}{4\left(\gamma^2(x-\xi)+\varphi^2\left(t-\frac{x}{V_c}\right)\right)}\right)} \qquad (2)$$

$$b = \frac{1}{2}\sqrt{\frac{V\pi}{LD_t}} \qquad (3)$$

$$\varphi = \sqrt{\frac{V}{D_t}} \qquad (4)$$

$$D_t = V\alpha_t + D_e \qquad (5)$$

$$D^* = n'^{(p)} D_o \qquad (6)$$

$$V_c = \frac{V}{R} \qquad (7)$$

$$R = 1 + \frac{\rho_b K_{oc} f_{oc}}{n} \qquad (8)$$

$$R' = 1 + \frac{\rho'_b K_{oc} f'_{oc}}{n'} \qquad (9)$$

$$\gamma = \frac{n'\sqrt{R'D^*}}{nD_t} \qquad (10)$$

where,

C'(x,z',t) = Aqueous concentration at lateral distance x, depth z′, and time t (M/L^3);
C_o = Mean plume loading concentration above the low-k layer during the charging period (M/L^3);
α_t = Coefficient of transverse hydrodynamic dispersion (L);
b = Source characteristic (1/L);
D^* = Effective transverse diffusion coefficient in the low-k layer (L^2/T);
D_e = Effective molecular diffusion coefficient in the transmissive layer (L^2/T);
D_o = Molecular diffusion coefficient in free water (L^2/T);
D_t = Effective transverse diffusion coefficient in the transmissive layer (L^2/T);
f_{oc} = Fraction organic carbon of the transmissive layer (unitless);
f'_{oc} = Fraction organic carbon of the low-k layer (unitless);
K_{oc} = Organic carbon partitioning coefficient (L^3/M);
L = Source zone length (L);
n = Porosity of transmissive layer (unitless);
n' = Porosity of low-k layer (unitless);
R = Retardation factors for the transmissive layer (unitless);
R' = Retardation factors for the low-k layer (unitless);
ρ_b = Bulk density of transmissive layer (M/L^3);
ρ'_b = Bulk density of low-k layer (M/L^3);
t = Time since source was introduced (T);
V = Seepage velocity in the transmissive layer (L/T);
V_c = Contaminant transport velocity in the transmissive layer (L/T);
x = Lateral distance from source edge (L);
ξ = Dummy integration variable; and
z' = Depth of the low-k layer (L).

Exhausted Source

Once the source is exhausted, the low-k aqueous concentration can be calculated at any time *t* using (Sale *et al*., 2008b):

$$C'(x,z',t,\tau) = C_o\left[\frac{1}{\sqrt{\pi}}\int_0^x\left(\frac{I_1(x,z',t,\xi)}{\sqrt{x-\xi}} - \frac{I_1(x,z',t-\tau,\xi)}{\sqrt{x-\xi}}\right)\left(\frac{1}{\sqrt{\pi\xi}} - \frac{b}{\varphi}e^{\frac{b^2\xi}{\varphi^2}}\operatorname{erfc}\left(\frac{b}{\varphi}\sqrt{\xi}\right)\right)d\xi\right] \quad (11)$$

where, τ is the source persistence time (i.e., the time in which the source is active) and $I_1(x,z',t-\tau,\xi)$ is defined as:

$$I_1(x,z',t-\tau,\xi) = \operatorname{erfc}\left(\frac{\frac{z'}{\sqrt{\frac{D^*}{R'}}}}{2\sqrt{t-\tau-\frac{x}{V_c}}}\right) - \gamma\frac{\operatorname{erfc}\left(\frac{\frac{\gamma z'}{\sqrt{\frac{D^*}{R'}}}}{2\left(t-\tau-\frac{x}{V_c}\right)\sqrt{\frac{\gamma^2}{t-\tau-\frac{x}{V_c}}+\frac{\varphi^2}{x-\xi}}}\right)}{\sqrt{t-\tau-\frac{x}{V_c}}\sqrt{\frac{\gamma^2}{t-\tau-\frac{x}{V_c}}+\frac{\varphi^2}{x-\xi}}\exp\left(\frac{\frac{\varphi^2 z'^2}{\left(\frac{D^*}{R'}\right)}}{4\left(\gamma^2(x-\xi)+\varphi^2\left(t-\tau-\frac{x}{V_c}\right)\right)}\right)} \quad (12)$$

Boundary Conditions

$$C'(x,z,0) = 0 \qquad (z \geq 0) \qquad (13)$$

$$C'(x,z',0) = 0 \qquad (-\infty < z' \leq 0) \qquad (14)$$

$$C'(x,z\to\infty,t) = 0 \quad (15)$$

$$C'(x,z'\to-\infty,t) = 0 \quad (16)$$

$$nD_t\frac{\partial C}{\partial z}(x,0,t) = n'D^*\frac{\partial C}{\partial z'}(x,0,t) \quad (17)$$

The source, introduced in the transmissive layer at x=0, is modeled as:

$$C'(0,z,t) = C_o e^{-bz}[1-H(t-\tau)] \quad (z \geq 0) \qquad (18)$$

where, C_o is the aqueous concentration at x=0, z=0, and H the Heaviside step function such that:

$$H(t-\tau) = \begin{cases} 0 \text{ if } t \leq \tau \\ 1 \text{ if } t > \tau \end{cases}$$

Numerical Integration Method

The Toolkit employs a 10-pt Gaussian quadrature to solve polynomials.

Appendix A.2.2. Low-k Sorbed Concentration

Purpose:
Determine the low-k sorbed concentration output in the Dandy-Sale Model of the Matrix Diffusion Toolkit.

Given:
The vertical plane source produces a plume in the transmissive zone that loads up the low-k zone due to diffusion. This vertical plane source is shut off and diffusion results in a release of contaminants from the low-k zone.

Assumptions:
The model makes the following assumptions:

1. A source, considered to be a thin pool, is introduced at the contact between the two layers upgradient of x=0.
2. A **loading period** occurs where there is a constant concentration of contaminants in the transmissive zone that drives contaminants into the low-k zone.
3. A **release period** occurs, where the transmissive zone is assumed to have no concentration, and an upper-range estimate of release from the low-k zone is generated.
4. There is no degradation in either layer.
5. Both layers are uniform, homogeneous, isotropic, and infinite in the z direction (perpendicular to groundwater flow).
6. One-dimensional (1-D) advective transport in the transmissive layer, parallel to the boundary of the layers, is accompanied by transverse dispersion and diffusion.
7. There is no longitudinal dispersion in the transmissive layer.
8. 1-D transverse diffusion transport occurs in the low-k layer.
9. Retardation of contaminants in both layers is based on instantaneous equilibrium between aqueous and sorbed phases.

Summary:
Active Source
Using a linear soil/water partitioning coefficient, the sorbed concentration in the low-k layer at any time *t* can be calculated as:

$$C'_{sorbed}(\mathrm{x}, \mathrm{z}', \mathrm{t}) = \mathrm{C}'(\mathrm{x}, \mathrm{z}', \mathrm{t})\, K_d \qquad (1)$$

where,

$C'_{sorbed}(x,z',t)$ = Sorbed concentration at lateral distance x, depth z′, and time t (M/M);
$C'(x,z',t)$ = Aqueous concentration at lateral distance x, depth z′, and time t (M/L^3) (calculated using Appendix A.2.1 Equation 1);
K_d = Soil/water partitioning coefficient (L^3/M);
= $f'_{oc}.K_{oc}$;
f'_{oc} = Fraction organic carbon of the low-k layer (unitless); and
K_{oc} = Organic carbon partitioning coefficient (L^3/M).

Exhausted Source

Once the source is exhausted, the low-k sorbed concentration can be calculated at any time *t* as:

$$C'_{sorbed}(\mathrm{x}, \mathrm{z}', \mathrm{t}, \tau) = \mathrm{C}'(\mathrm{x}, \mathrm{z}', \mathrm{t}, \tau) K_d \qquad (2)$$

where,

$C'_{sorbed}(x,z',t,\tau)$ = Sorbed concentration at lateral distance x, depth z′, and time t after the source has depleted (M/M); and

$C'(x,z',t,\tau)$ = Aqueous concentration at lateral distance x, depth z′, and time t after the source has depleted (M/L^3) (calculated using Appendix A.2.1 Equation 11).

Appendix A.2.3. Low-k Total Concentration

Purpose:
Determine the low-k total concentration output in the Dandy-Sale Model of the Matrix Diffusion Toolkit.

Given:
The vertical plane source produces a plume in the transmissive zone that loads up the low-k zone due to diffusion. This vertical plane source is shut off and diffusion results in a release of contaminants from the low-k zone.

Assumptions:
The model makes the following assumptions:

1. A source, considered to be a thin pool, is introduced at the contact between the two layers upgradient of x=0.
2. A **loading period** occurs where there is a constant concentration of contaminants in the transmissive zone that drives contaminants into the low-k zone.
3. A **release period** occurs, where the transmissive zone is assumed to have no concentration, and an upper-range estimate of release from the low-k zone is generated.
4. There is no degradation in either layer.
5. Both layers are uniform, homogeneous, isotropic, and infinite in the z direction (perpendicular to groundwater flow).
6. One-dimensional (1-D) advective transport in the transmissive layer, parallel to the boundary of the layers, is accompanied by transverse dispersion and diffusion.
7. There is no longitudinal dispersion in the transmissive layer.
8. 1-D transverse diffusion transport occurs in the low-k layer.
9. Retardation of contaminants in both layers is based on instantaneous equilibrium between aqueous and sorbed phases.

Summary:
Active Source
Since the medium is saturated with water, the water content equals the porosity. Consequently, the total concentration (mass of the constituent per unit bulk volume) can be obtained using:

$$C'_{total}(\mathrm{x},\mathrm{z}',\mathrm{t}) = \mathrm{C}'(\mathrm{x},\mathrm{z}',\mathrm{t})\left(\frac{n'+\rho'_b K_d}{\rho'_b}\right) \qquad (1)$$

where,

$C'_{total}(x,z',t)$ = Total concentration at lateral distance x, depth z′, and time t (M/M);
$C'(x,z',t)$ = Aqueous concentration at lateral distance x, depth z′, and time t (M/L^3) (calculated using Appendix A.2.1 Equation 1);
n' = Porosity of low-k layer (unitless);
ρ'_b = Bulk density of low-k layer (M/L^3);
K_d = Soil/water partitioning coefficient (L^3/M)

$= f'_{oc}.K_{oc}$;

f'_{oc} = Fraction organic carbon of the low-k layer (unitless); and

K_{oc} = Organic carbon partitioning coefficient (L^3/M).

Exhausted Source

Once the source is exhausted, the low-k total concentration can be calculated at any time *t* as:

$$C'_{total}(x, z', t, \tau) = C'(x, z', t, \tau)\left(\frac{n' + \rho'_b K_d}{\rho'_b}\right) \quad (2)$$

where,

$C'_{total}(x,z',t,\tau)$ = Total concentration at lateral distance x, depth z′, and time t after the source has depleted (M/M); and

$C'(x,z',t,\tau)$ = Aqueous concentration at lateral distance x, depth z′, and time t after the source has depleted (M/L^3) (calculated using Appendix A.2.1 Equation 11).

Appendix A.2.4. Low-k Aqueous Mass

Purpose:
Determine the low-k aqueous phase mass output in the Dandy-Sale Model of the Matrix Diffusion Toolkit.

Given:
The vertical plane source produces a plume in the transmissive zone that loads up the low-k zone due to diffusion. This vertical plane source is shut off and diffusion results in a release of contaminants from the low-k zone.

Assumptions:
The model makes the following assumptions:

1. A source, considered to be a thin pool, is introduced at the contact between the two layers upgradient of x=0.
2. A **loading period** occurs where there is a constant concentration of contaminants in the transmissive zone that drives contaminants into the low-k zone.
3. A **release period** occurs, where the transmissive zone is assumed to have no concentration, and an upper-range estimate of release from the low-k zone is generated.
4. There is no degradation in either layer.
5. Both layers are uniform, homogeneous, isotropic, and infinite in the z direction (perpendicular to groundwater flow).
6. One-dimensional (1-D) advective transport in the transmissive layer, parallel to the boundary of the layers, is accompanied by transverse dispersion and diffusion.
7. There is no longitudinal dispersion in the transmissive layer.
8. 1-D transverse diffusion transport occurs in the low-k layer.
9. Retardation of contaminants in both layers is based on instantaneous equilibrium between aqueous and sorbed phases.

Summary:
Active Source
Aqueous phase mass in the low-k layer at any time *t* can be calculated as:

$$M'_{aq}(\mathrm{t}) = \sum_i^N \mathrm{C}'(\mathrm{x},\mathrm{z}',\mathrm{t}) l' W h' n' \qquad (1)$$

where,

$M'_{aq}(t)$ = Aqueous phase mass in the low-k layer at time t (M);
$C'(x,z',t)$ = Aqueous concentration at lateral distance x, depth z′, and time t (M/L^3) (calculated using Appendix A.2.1 Equation 1);
i = Cell of the concentration in the lateral distance from the source vs. depth in low-k output array;
N = Total number of cells in the output array;
l' = Length of cell in the concentration in the lateral distance from the source vs. depth in low-k output array (L);

h′ = Height of cell in the concentration in the lateral distance from the source vs. depth in low-k output array (L);
n′ = Porosity of low-k layer (unitless); and
W = Source zone width (L).

Exhausted Source

Once the source is exhausted, the low-k aqueous phase mass can be calculated at any time *t* as:

$$M'_{aq}(\mathrm{t},\tau) = \sum_i^N \mathrm{C}'(\mathrm{x},\mathrm{z}',\mathrm{t},\tau) l' W h' n' \quad (2)$$

where,

$M'_{aq}(t,\tau)$ = Aqueous phase mass at time t after the source has depleted (M); and
$C'(x,z',t,\tau)$ = Aqueous concentration at lateral distance x, depth z′, and time t after the source has depleted (M/L^3) (calculated using Appendix A.2.1 Equation 11).

Appendix A.2.5. Low-k Sorbed Mass

Purpose:
Determine the low-k sorbed phase mass output in the Dandy-Sale Model of the Matrix Diffusion Toolkit.

Given:
The vertical plane source produces a plume in the transmissive zone that loads up the low-k zone due to diffusion. This vertical plane source is shut off and diffusion results in a release of contaminants from the low-k zone.

Assumptions:
The model makes the following assumptions:

1. A source, considered to be a thin pool, is introduced at the contact between the two layers upgradient of x=0.
2. A **loading period** occurs where there is a constant concentration of contaminants in the transmissive zone that drives contaminants into the low-k zone.
3. A **release period** occurs, where the transmissive zone is assumed to have no concentration, and an upper-range estimate of release from the low-k zone is generated.
4. There is no degradation in either layer.
5. Both layers are uniform, homogeneous, isotropic, and infinite in the z direction (perpendicular to groundwater flow).
6. One-dimensional (1-D) advective transport in the transmissive layer, parallel to the boundary of the layers, is accompanied by transverse dispersion and diffusion.
7. There is no longitudinal dispersion in the transmissive layer.
8. 1-D transverse diffusion transport occurs in the low-k layer.
9. Retardation of contaminants in both layers is based on instantaneous equilibrium between aqueous and sorbed phases.

Summary:
Active Source
Sorbed phase mass in the low-k layer at any time *t* can be calculated as:

$$M'_s(\mathrm{t}) = M'_{aq}(\mathrm{t})\left(\frac{\rho'_b K_d}{n'}\right) \qquad (1)$$

where,

$M'_s(t)$ = Sorbed phase mass in the low-k layer at time t (M);
$M'_{aq}(t)$ = Aqueous phase mass in the low-k layer at time t (M) (calculated using Appendix A.2.4 Equation 1);
n' = Porosity of low-k layer (unitless);
ρ'_b = Bulk density of low-k layer (M/L^3);
K_d = Soil/water partitioning coefficient (L^3/M)
= $f'_{oc}.K_{oc}$;
f'_{oc} = Fraction organic carbon of the low-k layer (unitless); and

K_{oc} = Organic carbon partitioning coefficient (L^3/M).

Exhausted Source

Once the source is exhausted, the low-k sorbed phase mass can be calculated at any time *t* as:

$$M'_s(t,\tau) = M'_{aq}(t,\tau)\left(\frac{\rho'_b K_d}{n'}\right) \quad (2)$$

where,

$M'_s(t,\tau)$ = Sorbed phase mass at time t after the source has depleted (M); and

$M'_{aq}(t,\tau)$ = Aqueous phase mass at time t after the source has depleted (M) (calculated using Appendix A.2.4 Equation 2).

Appendix A.2.6. Low-k Total Mass

Purpose:
Determine the low-k total mass output in the Dandy-Sale Model of the Matrix Diffusion Toolkit.

Given:
The vertical plane source produces a plume in the transmissive zone that loads up the low-k zone due to diffusion. This vertical plane source is shut off and diffusion results in a release of contaminants from the low-k zone.

Assumptions:
The model makes the following assumptions:

1. A source, considered to be a thin pool, is introduced at the contact between the two layers upgradient of x=0.
2. A **loading period** occurs where there is a constant concentration of contaminants in the transmissive zone that drives contaminants into the low-k zone.
3. A **release period** occurs, where the transmissive zone is assumed to have no concentration, and an upper-range estimate of release from the low-k zone is generated.
4. There is no degradation in either layer.
5. Both layers are uniform, homogeneous, isotropic, and infinite in the z direction (perpendicular to groundwater flow).
6. One-dimensional (1-D) advective transport in the transmissive layer, parallel to the boundary of the layers, is accompanied by transverse dispersion and diffusion.
7. There is no longitudinal dispersion in the transmissive layer.
8. 1-D transverse diffusion transport occurs in the low-k layer.
9. Retardation of contaminants in both layers is based on instantaneous equilibrium between aqueous and sorbed phases.

Summary:
Active Source
Total mass in the low-k layer at any time *t* can be calculated as:

$$M'_{tot}(\mathrm{t}) = M'_{aq}(\mathrm{t}) + M'_{s}(\mathrm{t}) \qquad (1)$$

where,

$M'_{tot}(t)$ = Total mass in the low-k layer at time t (M);
$M'_{aq}(t)$ = Aqueous phase mass in the low-k layer at time t (M) (calculated using Appendix A.2.4 Equation 1); and
$M'_{s}(t)$ = Sorbed phase mass in the low-k layer at time t (M) (calculated using Appendix A.2.5 Equation 1).

Exhausted Source
Once the source is exhausted, the low-k total mass can be calculated at any time *t* as:

$$M'_{tot}(t,\tau) = M'_{aq}(t,\tau) + M'_{s}(t,\tau) \qquad (2)$$

where,

$M'_{tot}(t,\tau)$ = Total mass at time t after the source has depleted (M);

$M'_{aq}(t,\tau)$ = Aqueous phase mass at time t after the source has depleted (M) (calculated using Appendix A.2.4 Equation 2); and

$M'_{s}(t,\tau)$ = Sorbed phase mass at time t after the source has depleted (M) (calculated using Appendix A.2.5 Equation 2).

Appendix A.2.7. Transmissive Layer Aqueous Concentration

Purpose:
Determine the transmissive layer aqueous concentration output in the Dandy-Sale Model of the Matrix Diffusion Toolkit. Note: This derivation was originally developed by Sale *et al*. (2008b) and described in detail in Sale *et al*. (2008b) and Bolhari (2012).

Given:
The vertical plane source produces a plume in the transmissive zone that loads up the low-k zone due to diffusion. This vertical plane source is shut off and diffusion results in a release of contaminants from the low-k zone.

Assumptions:
The Toolkit uses a simplified conceptual model of a two-layer aquifer system, a transmissive layer above a low-k layer (Figure A.2.7.1). A source (e.g., DNAPL) is introduced at the contact between the two layers. As shown in the figure, x is in the direction of groundwater flow, and z the direction perpendicular to groundwater flow. The edge of the source, at the interface between the two layers, is designated x=0 and z=0, with both x and z increasing with distance away from the source edge. In this model, z' is designated as the vertical depth from the source in the low-k layer, and z the height in the transmissive zone.

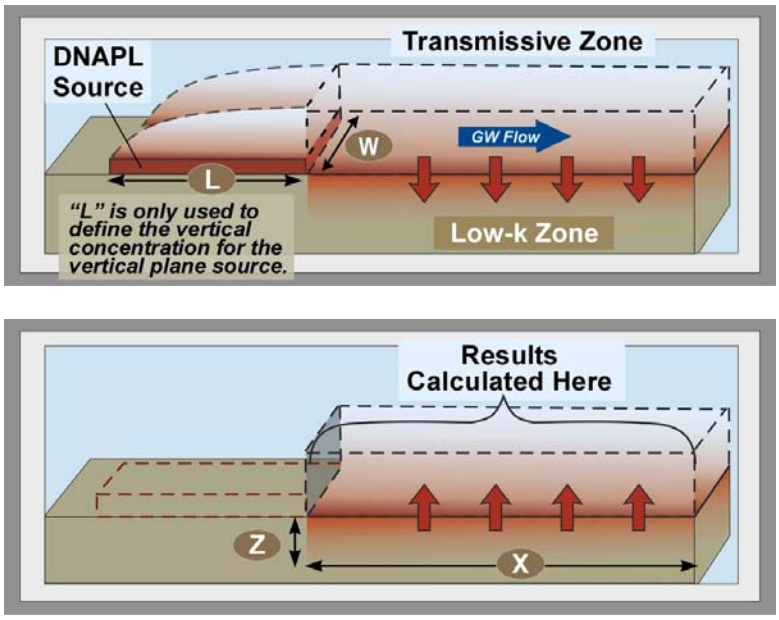

Figure A.2.7.1. The two-layer scenario conceptual model: Top) Active Source, Bottom) Depleted Source

The model makes the following assumptions:

1. A source, considered to be a thin pool, is introduced at the contact between the two layers upgradient of x=0.

2. A **loading period** occurs where there is a constant concentration of contaminants in the transmissive zone that drives contaminants into the low-k zone.
3. A **release period** occurs, where the transmissive zone is assumed to have no concentration, and an upper-range estimate of release from the low-k zone is generated.
4. There is no degradation in either layer.
5. Both layers are uniform, homogeneous, isotropic, and infinite in the z direction (perpendicular to groundwater flow).
6. One-dimensional (1-D) advective transport in the transmissive layer, parallel to the boundary of the layers, is accompanied by transverse dispersion and diffusion.
7. There is no longitudinal dispersion in the transmissive layer.
8. 1-D transverse diffusion transport occurs in the low-k layer.
9. Retardation of contaminants in both layers is based on instantaneous equilibrium between aqueous and sorbed phases.

Summary:
In 2008b, Sale *et al*. developed Equation 1 to calculate the concentration in the transmissive zone with an active source:

$$c_{trans}(x,z,t) = c_o \left[\frac{1}{2} e^{\frac{b^2 x}{\varphi^2}} \left(e^{bz} \operatorname{erfc}\left(\frac{b}{\varphi}\sqrt{x} + \frac{\varphi z}{2\sqrt{x}} \right) + e^{-bz} + e^{-bz} \operatorname{erf}\left(\frac{-b}{\varphi}\sqrt{x} + \frac{\varphi z}{2\sqrt{x}} \right) \right) - \frac{\varphi z}{\pi} e^{bz} \sqrt{t - \frac{x}{v_c}} \int_0^x \frac{e^{\frac{b^2 \xi}{\varphi^2}}}{\sqrt{x-\xi}} \left(\frac{\operatorname{erfc}\left(\frac{b}{\varphi}\sqrt{\xi} + \frac{\varphi z}{2\sqrt{\xi}} \right)}{\gamma^2 (x-\xi) + \varphi^2 \left(t - \frac{x}{v_c} \right)} \right) d\xi \right] \quad (1)$$

However, as demonstrated by Bolhari (2012), the above equation has a finite domain of application (<100 meters). Consequently, the Toolkit estimates the transmissive zone aqueous concentrations by determining the flux across the low-k/transmissive zone interface and assuming discharge to a hypothetical well with a 10-ft (3-m) screened interval.

This 10-foot screened interval was selected because at an actual field site, contamination diffusing from a low-k zone might spread vertically above a 1-foot screen. It was thought to be very unlikely that there would be more than 10 feet of vertical spreading in the transmissive zone. Bottom line: the 10-foot screened interval is hard-wired into the model and cannot be changed.

Due to computational limitations, all transmissive zone solutions show increasing numerical imprecision for lengths greater than 1500 m. Therefore, we recommend limiting the lateral distance from the source to **≤ 1500 m** for any model runs involving transmissive zone solutions.

If you are sure all the mass discharge is being captured by a well with a different screened interval, you can get the modeled concentration in this well by multiplying the model output by the ratio of the screens (your screened interval ÷ 10 feet).

Contaminant flux at the layer interface can be derived by obtaining the derivative of concentration in the low-k zone with respect to z′ at z′=0.

Active Source

Contaminant mass flux across the low-k/transmissive layer boundary at any lateral distance from the source and time can be obtained from:

$$J_y(x,t) = -C_o n' \sqrt{\frac{VR'D^*}{\pi D_t}} \sqrt{t - \frac{x}{V_c}} \left[\frac{-1}{\sqrt{\gamma^2 x\left(t-\frac{x}{V_c}\right)+\varphi^2\left(t-\frac{x}{V_c}\right)^2}} + \frac{b}{\sqrt{\pi}} \int_0^x \frac{e^{\frac{b^2\xi}{\varphi^2}}}{\sqrt{x-\xi}} \left(\frac{\operatorname{erfc}\left(\frac{b}{\varphi}\sqrt{\xi}\right)}{\gamma^2(x-\xi)+\varphi^2\left(t-\frac{x}{V_c}\right)} \right) d\xi \right] \qquad (2)$$

with b, φ, D_t, D^*, V_c, R, R', and γ:

$$b = \frac{1}{2}\sqrt{\frac{V\pi}{LD_t}} \qquad (3)$$

$$\varphi = \sqrt{\frac{V}{D_t}} \qquad (4)$$

$$D_t = V\alpha_t + D_e \qquad (5)$$

$$D^* = n'^{(p)} D_o \qquad (6)$$

$$V_c = \frac{V}{R} \qquad (7)$$

$$R = 1 + \frac{\rho_b K_{oc} f_{oc}}{n} \qquad (8)$$

$$R' = 1 + \frac{\rho'_b K_{oc} f'_{oc}}{n'} \qquad (9)$$

$$\gamma = \frac{n'\sqrt{R'D^*}}{nD_t} \qquad (10)$$

where,

- $J_y(x,t)$ = Contaminant flux at distance x and time t (M/T);
- C_o = Mean plume loading concentration above the low-k layer during the charging period (M/L^3);
- α_t = Coefficient of transverse hydrodynamic dispersion (L);
- b = Source characteristic (1/L);
- D^* = Effective transverse diffusion coefficient in the low-k layer (L^2/T);
- D_e = Effective molecular diffusion coefficient in the transmissive layer (L^2/T);
- D_o = Molecular diffusion coefficient in free water (L^2/T);

D_t = Effective transverse diffusion coefficient in the transmissive layer (L^2/T);
f_{oc} = Fraction organic carbon of the transmissive layer (unitless);
f'_{oc} = Fraction organic carbon of the low-k layer (unitless);
K_{oc} = Organic carbon partitioning coefficient (L^3/M);
L = Source zone length (L);
n = Porosity of transmissive layer (unitless);
n' = Porosity of low-k layer (unitless);
R = Retardation factors for the transmissive layer (unitless);
R' = Retardation factors for the low-k layer (unitless);
t = Time since source was introduced (T);
V = Seepage velocity in the transmissive layer (L/T);
V_c = Contaminant transport velocity in the transmissive layer (L/T);
x = Lateral distance from source edge (L); and
ξ = Dummy integration variable.

Positive mass flux values indicate diffusion from the transmissive zone into the low-k zone. Negative values indicate diffusion from the low-k zone into the transmissive zone. While the source is on, diffusion will occur from the transmissive zone into the low-k zone.

Concentration in the transmissive layer can be estimated by imagining the contaminant plume as a train car, picking up initial mass from the source and losing mass to the low-k layer through diffusion as shown on Figure A.2.7.2.

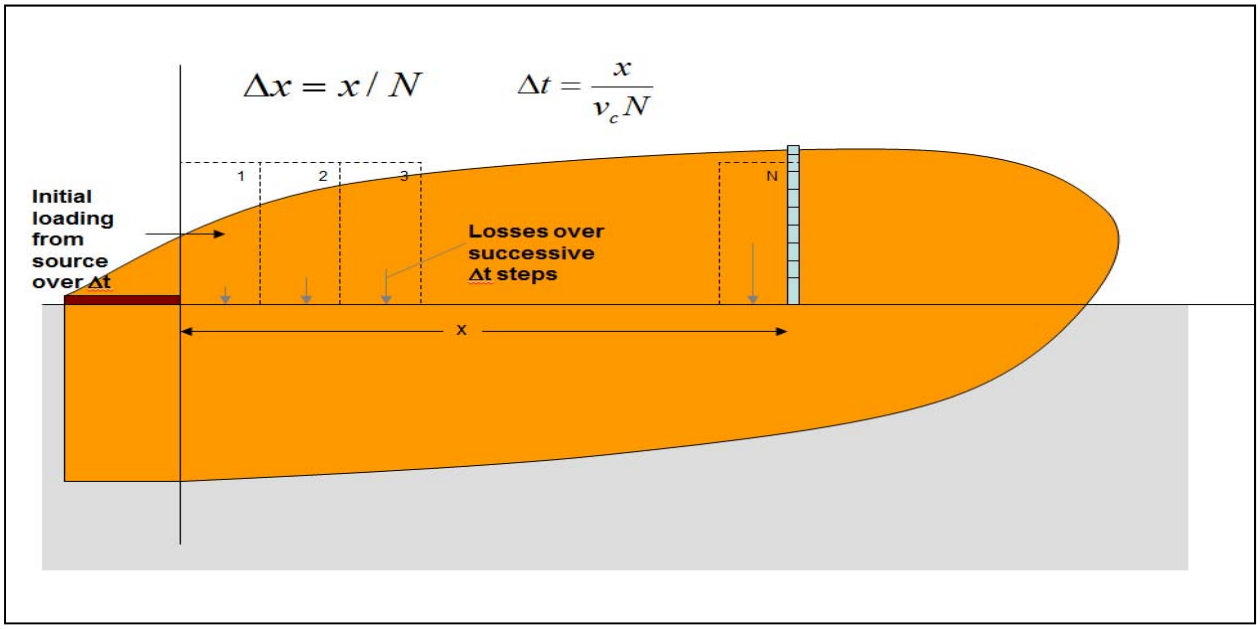

Figure A.2.7.2. Schematic for calculating concentration in the transmissive zone.

Concentrations are calculated using the following steps:

1. Assume a monitoring well with a 10-ft (3-m) screened interval located at the distance *x* of interest.

2. Set well concentration to zero if point of interest is greater than the point of plume arrival (i.e., $x \geq V_c t$, where V_c is the contaminant velocity in the transmissive layer and *t* the time of interest).
3. Otherwise, divide the spatial distance *x* into *N* subdivisions.
4. Calculate:

$$\Delta x = \frac{x}{N}$$

5. Calculate:

$$\Delta t = \frac{x}{V_c N}$$

6. Determine the initial mass loaded onto the reference volume over the time period *Δt*:

$$M_{remain} = \frac{C_o}{b} VWn\Delta t$$

where, *W* is the source zone width.

7. Loop estimated losses from the reference volume over the *N* spatial subdivision. That is, for *i* = 1 to *N* repeat:
    a. Determine the midpoint for each spatial subdivision:

$$xx = (i-1)\Delta x + \frac{\Delta x}{2}$$

    b. Determine the midpoint of the mass lost to the low-k zone at each spatial subdivision:

$$tt = t - \left[(N-i)\Delta t - \frac{\Delta t}{2}\right]$$

    c. Using Equation 2, calculate the flux across the interface at spatial location *xx* and time *tt*.
    d. Remove mass from the reference volume at each spatial subdivision over the period Δt:

$$M_{remain} = M_{remain} - J_y(xx, tt)\Delta x W \Delta t$$

    e. Calculate the concentration in the hypothetical well, by dividing the mass remaining by the volume of water in the reference volume:

$$\mathrm{C_{well}} = \frac{\mathrm{M_{remain}}}{\mathrm{RW\Delta xh_w n}}$$

where, h_w is the screen interval of the well.

8. The concentration in the transmissive layer at distance *x* and time *t* = C_{well} at *i* = *N*.

Exhausted Source

Concentration in the transmissive zone after the source is exhausted can be determined using the principle of superposition. For this purpose:

1. Well concentration is calculated for time = *t* using steps 1 through 8 above.
2. Well concentration is calculated for time $t > \tau$ (where τ is the source persistence time, i.e., the time in which the source is active) as:
    a. Assume a monitoring well with a 10-ft (3-m) screened interval located at the distance *x* of interest.
    b. Divide the spatial distance *x* into *N* subdivisions.
    c. Calculate:

$$\Delta x = \frac{x}{N}$$

    d. Calculate:

$$\Delta t = \frac{x}{V_c N}$$

    e. Determine the initial mass loaded onto the reference volume over the time period *Δt*::

$$M_{remain} = \frac{C_o}{b} VWn\Delta t$$

    where, *W* is the source zone width.
    f. Loop estimated losses from the reference volume over the *N* spatial subdivision. That is, for *i* = 1 to *N* repeat:
        a. Determine the midpoint for each spatial subdivision:

$$xx = (i-1)\Delta x + \frac{\Delta x}{2}$$

        b. Determine the midpoint of the mass lost to the low-k zone at each spatial subdivision:

            i. For $x \geq V_c(t-\tau)$:

$$tt = t + \left(\frac{xx - x}{V_c}\right)$$

            ii. For $x < V_c(t-\tau)$:

$$tt = t - \tau + \left(\frac{xx - x}{V_c}\right)$$

        c. Using Equation 2, calculate the flux across the interface at spatial location *xx* and time *tt*.
        d. Remove mass from the reference volume at each spatial subdivision over the period Δt:

$$M_{remain} = M_{remain} - J_y(xx, tt)\Delta x W \Delta t$$

e. Calculate the concentration in the hypothetical well, by dividing the mass remaining by the volume of water in the reference volume:

$$C_{well} = \frac{M_{remain}}{RW\Delta x h_w n}$$

where h_w is the screen interval of the well.

g. The concentration in the transmissive layer at distance *x* and time *t* = C_{well} at *i* = *N*.

3. Well concentration at time *t* after the source is exhausted is obtained by subtracting the well concentration calculated in Step 2 from Step 1.

Numerical Integration Method

The Matrix Diffusion Toolkit employs a 10-pt Gaussian quadrature to solve polynomials.

Appendix A.2.8. Transmissive Layer Sorbed Concentration

Purpose:
Determine the transmissive layer sorbed concentration output in the Dandy-Sale Model of the Matrix Diffusion Toolkit.

Given:
The vertical plane source produces a plume in the transmissive zone that loads up the low-k zone due to diffusion. This vertical plane source is shut off and diffusion results in a release of contaminants from the low-k zone.

Assumptions:
The model makes the following assumptions:

1. A source, considered to be a thin pool, is introduced at the contact between the two layers upgradient of x=0.
2. A **loading period** occurs where there is a constant concentration of contaminants in the transmissive zone that drives contaminants into the low-k zone.
3. A **release period** occurs, where the transmissive zone is assumed to have no concentration, and an upper-range estimate of release from the low-k zone is generated.
4. There is no degradation in either layer.
5. Both layers are uniform, homogeneous, isotropic, and infinite in the z direction (perpendicular to groundwater flow).
6. One-dimensional (1-D) advective transport in the transmissive layer, parallel to the boundary of the layers, is accompanied by transverse dispersion and diffusion.
7. There is no longitudinal dispersion in the transmissive layer.
8. 1-D transverse diffusion transport occurs in the low-k layer.
9. Retardation of contaminants in both layers is based on instantaneous equilibrium between aqueous and sorbed phases.

Summary:
Using a linear soil/water partitioning coefficient, the sorbed concentration in the low-k layer at any time *t* can be calculated as:

$$C_{sorbed}(\mathrm{x,t}) = \mathrm{C}_{well}\, K_d \qquad (1)$$

where,

$C_{sorbed}(x,t)$ = Sorbed concentration at lateral distance *x* and any time *t* (M/M);
C_{well} = Well concentration at lateral distance x and any time t (M/L^3) (calculated using Appendix A.2.7);
K_d = Soil/water partitioning coefficient (L^3/M)
= $f_{oc}.K_{oc}$;
f_{oc} = Fraction organic carbon of the transmissive layer (unitless); and
K_{oc} = Organic carbon partitioning coefficient (L^3/M).

Appendix A.2.9. Transmissive Layer Total Concentration

Purpose:
Determine the transmissive layer total concentration output in the Dandy-Sale Model of the Matrix Diffusion Toolkit.

Given:
The vertical plane source produces a plume in the transmissive zone that loads up the low-k zone due to diffusion. This vertical plane source is shut off and diffusion results in a release of contaminants from the low-k zone.

Assumptions:
The model makes the following assumptions:

1. A source, considered to be a thin pool, is introduced at the contact between the two layers upgradient of x=0.
2. A **loading period** occurs where there is a constant concentration of contaminants in the transmissive zone that drives contaminants into the low-k zone.
3. A **release period** occurs, where the transmissive zone is assumed to have no concentration, and an upper-range estimate of release from the low-k zone is generated.
4. There is no degradation in either layer.
5. Both layers are uniform, homogeneous, isotropic, and infinite in the z direction (perpendicular to groundwater flow).
6. One-dimensional (1-D) advective transport in the transmissive layer, parallel to the boundary of the layers, is accompanied by transverse dispersion and diffusion.
7. There is no longitudinal dispersion in the transmissive layer.
8. 1-D transverse diffusion transport occurs in the low-k layer.
9. Retardation of contaminants in both layers is based on instantaneous equilibrium between aqueous and sorbed phases.

Summary:
Since the medium is saturated with water, the water content equals the porosity. Consequently, the total concentration (mass of the constituent per unit bulk volume) can be obtained using:

$$C_{total}(\mathrm{x},\mathrm{t}) = \mathrm{C}_{well}\left(\frac{n+\rho_b K_d}{\rho_b}\right) \qquad (1)$$

where,

$C_{total}(x,t)$ = Total concentration at lateral distance x and any time t (M/M);
C_{well} = Well concentration at lateral distance x and any time t (M/L^3) (calculated using Appendix A.2.7);
n = Porosity of transmissive layer (unitless);
ρ_b = Bulk density of transmissive layer (M/L^3);
K_d = Soil/water partitioning coefficient (L^3/M)
= $f_{oc}.K_{oc}$;

f_{oc} = Fraction organic carbon of the transmissive layer (unitless); and
K_{oc} = Organic carbon partitioning coefficient (L^3/M).

Appendix A.2.10. Transmissive Layer Aqueous Mass

Purpose:
Determine the transmissive layer aqueous phase mass output in the Dandy-Sale Model of the Matrix Diffusion Toolkit.

Given:
The vertical plane source produces a plume in the transmissive zone that loads up the low-k zone due to diffusion. This vertical plane source is shut off and diffusion results in a release of contaminants from the low-k zone.

Assumptions:
The model makes the following assumptions:

1. A source, considered to be a thin pool, is introduced at the contact between the two layers upgradient of x=0.
2. A **loading period** occurs where there is a constant concentration of contaminants in the transmissive zone that drives contaminants into the low-k zone.
3. A **release period** occurs, where the transmissive zone is assumed to have no concentration, and an upper-range estimate of release from the low-k zone is generated.
4. There is no degradation in either layer.
5. Both layers are uniform, homogeneous, isotropic, and infinite in the z direction (perpendicular to groundwater flow).
6. One-dimensional (1-D) advective transport in the transmissive layer, parallel to the boundary of the layers, is accompanied by transverse dispersion and diffusion.
7. There is no longitudinal dispersion in the transmissive layer.
8. 1-D transverse diffusion transport occurs in the low-k layer.
9. Retardation of contaminants in both layers is based on instantaneous equilibrium between aqueous and sorbed phases.

Summary:
Aqueous phase mass in the low-k layer at any time *t* can be calculated as:

$$M_{aq}(\mathrm{t}) = \sum_{i=1}^{N} C_{well} l W h_w n$$

where,

$M_{aq}(t)$ = Aqueous phase mass in the transmissive layer at any time t (M);
C_{well} = Well concentration at lateral distance x and any time t (M/L^3) (calculated using Appendix A.2.7);
N = Total number of wells in the output graph (i.e., intervals on x-axis of graph);
l = Distance to midpoint on each side of well (L);
h_w = Screen interval of well (L); and
n = Porosity of transmissive layer (unitless).

Appendix A.2.11. Transmissive Layer Sorbed Mass

Purpose:
Determine the transmissive layer sorbed phase mass output in Dandy-Sale Model of the Matrix Diffusion Toolkit.

Given:
The vertical plane source produces a plume in the transmissive zone that loads up the low-k zone due to diffusion. This vertical plane source is shut off and diffusion results in a release of contaminants from the low-k zone.

Assumptions:
The model makes the following assumptions:

1. A source, considered to be a thin pool, is introduced at the contact between the two layers upgradient of x=0.
2. A **loading period** occurs where there is a constant concentration of contaminants in the transmissive zone that drives contaminants into the low-k zone.
3. A **release period** occurs, where the transmissive zone is assumed to have no concentration, and an upper-range estimate of release from the low-k zone is generated.
4. There is no degradation in either layer.
5. Both layers are uniform, homogeneous, isotropic, and infinite in the z direction (perpendicular to groundwater flow).
6. One-dimensional (1-D) advective transport in the transmissive layer, parallel to the boundary of the layers, is accompanied by transverse dispersion and diffusion.
7. There is no longitudinal dispersion in the transmissive layer.
8. 1-D transverse diffusion transport occurs in the low-k layer.
9. Retardation of contaminants in both layers is based on instantaneous equilibrium between aqueous and sorbed phases.

Summary:
Sorbed phase mass in the transmissive layer at any time *t* can be calculated as:

$$M_s(\mathrm{t}) = M_{aq}(\mathrm{t})\left(\frac{\rho_b K_d}{n}\right)$$

where,

$M_s(t)$ = Sorbed phase mass in the transmissive layer at any time *t* (M);
$M_{aq}(t)$ = Aqueous phase mass in the low-k layer at time *t* (M) (calculated using Appendix A.2.10);
n = Porosity of transmissive layer (unitless);
ρ_b = Bulk density of transmissive layer (M/L^3);
K_d = Soil/water partitioning coefficient (L^3/M)
= $f_{oc}.K_{oc}$;
f_{oc} = Fraction organic carbon of the transmissive layer (unitless); and
K_{oc} = Organic carbon partitioning coefficient (L^3/M).

Appendix A.2.12. Transmissive Layer Total Mass

Purpose:
Determine the transmissive layer total mass output in the Dandy-Sale Model of the Matrix Diffusion Toolkit.

Given:
There is a finite amount of soluble organic constituents in the source zone (in the dissolved, sorbed, and NAPL phases).

Assumptions:
The model makes the following assumptions:

1. A source, considered to be a thin pool, is introduced at the contact between the two layers upgradient of x=0.
2. A **loading period** occurs where there is a constant concentration of contaminants in the transmissive zone that drives contaminants into the low-k zone.
3. A **release period** occurs, where the transmissive zone is assumed to have no concentration, and an upper-range estimate of release from the low-k zone is generated.
4. There is no degradation in either layer.
5. Both layers are uniform, homogeneous, isotropic, and infinite in the z direction (perpendicular to groundwater flow).
6. One-dimensional (1-D) advective transport in the transmissive layer, parallel to the boundary of the layers, is accompanied by transverse dispersion and diffusion.
7. There is no longitudinal dispersion in the transmissive layer.
8. 1-D transverse diffusion transport occurs in the low-k layer.
9. Retardation of contaminants in both layers is based on instantaneous equilibrium between aqueous and sorbed phases.

Summary:
Total mass in the transmissive layer at any time *t* can be calculated as:

$$M_{tot}(\mathrm{t}) = M_{aq}(\mathrm{t}) + M_s(\mathrm{t})$$

where,

$M_{tot}(t)$ = Total mass in the transmissive layer at any time t (M);
$M_{aq}(t)$ = Aqueous phase mass in the transmissive layer at any time *t* (M) (calculated using Appendix A.2.10); and
$M_s(t)$ = Sorbed phase mass in the transmissive layer at any time *t* (M) (calculated using Appendix A.2.11).

APPENDIX A.3. PROBABILITY DISTRIBUTIONS

This section describes in greater detail the probability distributions employed in the Monte Carlo analysis. The Matrix Diffusion Toolkit offers the user three distribution options: normal, lognormal, and uniform.

A.3.1 Normal Distributions

Normal distributions are defined by the density function:

$$f(x) = \frac{1}{\sigma\sqrt{2\pi}} e^{-\left(\frac{(x-\mu)^2}{2\sigma^2}\right)} \qquad -\infty < x < \infty$$

where, σ is the standard deviation and μ the mean of the distribution. The Toolkit assumes that the values entered in the "Input Data and Grid" screen are the means. The uncertainty analysis requires the user to specify a σ as a percentage of the mean.

A.3.2 Lognormal Distributions

A lognormal distribution is a distribution whose logarithms are normally distributed. The lognormal density function is:

$$f(x) = \frac{1}{x\sigma\sqrt{2\pi}} e^{-\left(\frac{(\ln(x)-\mu)^2}{2\sigma^2}\right)} \qquad x, \sigma > 0$$

where, σ is the standard deviation and μ the mean of the underlying normal distribution.

Lognormal distributions are typically specified in two ways throughout literature (Swiler and Wyss, 2004). One way, as described above, is to use the mean and standard deviation of the underlying normal distribution. The other way is to use the mean of the lognormal distribution (α) and a term called the "Error Factor." For a lognormal distribution, the error factor is the ratio of the 95th percentile to the median, or equivalently, the ratio of the median to the 5th percentile. Therefore, the error factor represents the width of a 90% confidence interval around the median.

In terms of the error factor, the relationship between the underlying normal distribution and the lognormal distribution can be described by:

$$\sigma = \ln(\text{error factor})/1.645$$

and

$$\mu = \ln(\alpha) - \frac{\sigma^2}{2}$$

where, α is the mean of the lognormal distribution, and σ and μ the standard deviation and mean of the underlying normal distribution, respectively.

The Toolkit describes the lognormal distribution using the error factor.

A.3.3 Uniform Distributions

A uniform distribution is specified over a particular interval and implies that all the points within that interval have equal probability of occurring. The uniform probability distribution function is:

$$f(x) = \frac{1}{B - A} \qquad A \leq x \leq B$$

where, A and B are the lower and upper bounds, respectively.

CASE STUDIES

CASE STUDY 1. INDUSTRIAL SITE, CONNECTICUT

Overview:

The Matrix Diffusion Toolkit was used to estimate the effects of diffusion into and from low-k zones for the trichloroethene (TCE) plume at an industrial site in Connecticut (Figure 1.1). Chapman and Parker (2005) have described the site in detail.

For this analysis, both the Square Root Model (SRM) (Case Study 1A) and the Dandy-Sale Model (DSM) (Case Study 1B) were applied as follows:

- Step 1: Initial values of all parameters, obtained from either Chapman and Parker (2005) or default Matrix Diffusion Toolkit parameters, were entered into the Toolkit.
- Step 2. Toolkit outputs were compared to field-observed TCE concentrations. This step was critical in determining how well default Toolkit parameters predicted actual field conditions.
- Step 3. Input parameters were adjusted, as needed, to improve the comparison with field-observed TCE concentrations.

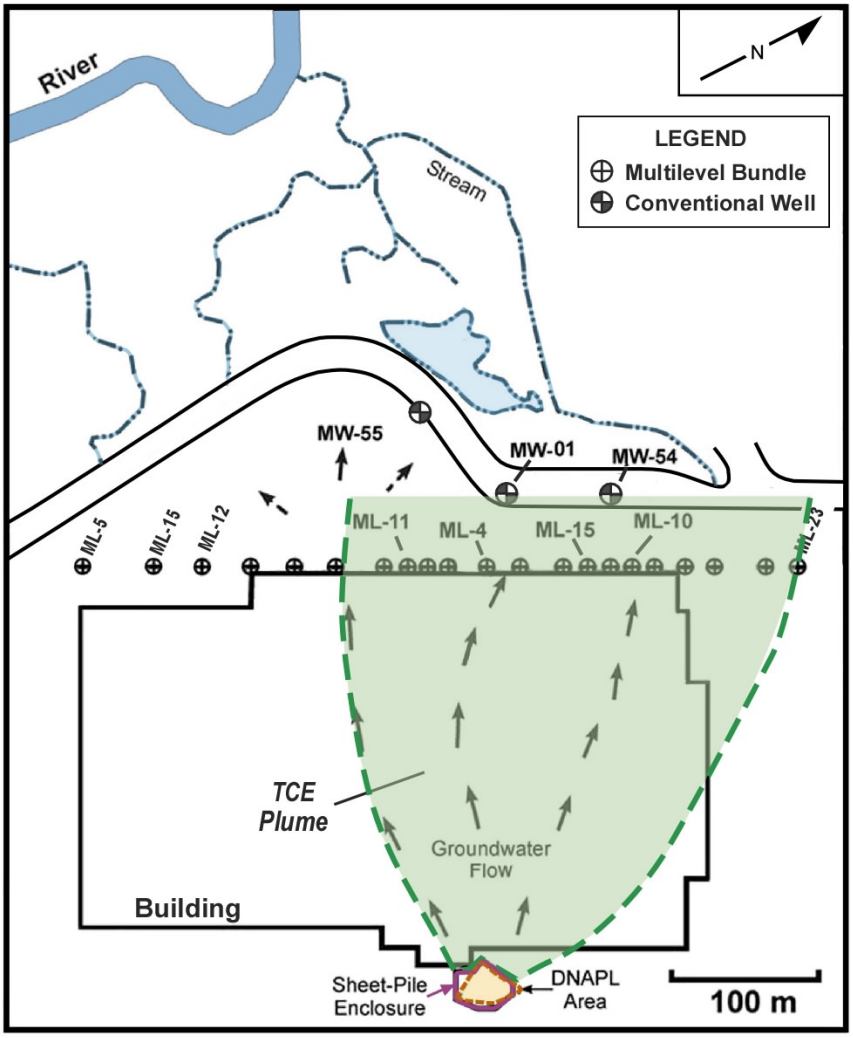

Figure 1.1. Site Location Map. Based on Chapman and Parker (2005) Figure 1.

A. Square Root Model

SRM Input Data:

Data Type	Parameter	Value	Source of Data
Hydrogeology	• Low-k zone description: • Low-k zone porosity: • Darcy velocity:	silt 0.43 (-) 0.13 (m/d)	• Boring logs • Estimated • Calculated
Transport – Low-k Zone	• Key constituent: • Molecular diffusion coefficient in free water: • Apparent tortuosity factor exponent: • Retardation factor:	TCE 9.1E-10 (m^2/sec) 0.33 (-) 1.2 (-)	• Site history • Literature (Toolkit default) • Literature (Toolkit default) • Calculated using measured faction organic carbon
Plume Characteristics	• High concentration zone • Approximate length: • Approximate width: • Highest concentration in black box: • Concentration of contour line in black box: • Representative concentration: • Next highest concentration zone • Approximate length: • Approximate width: • Concentration of contour line in blue box: • Representative concentration: • Uncertainty in plume concentration estimations:	 330 (m) 300 (m) 37,000 (µg/L) 37,000 (µg/L) 37,000 (µg/L) 330 (m) 300 (m) 37,000 (µg/L) 37,000 (µg/L) 10 (± factor of)	• Based on area of affected groundwater plume • Same as black box.
General	• Source loading starts in year: • Source removed in year:	1952 1996	• Site history • Site history
Field Data for Comparison	• TCE Concentration in MW-01 (transmissive zone)	Year / Conc. (µg/L): 1998 3,832 1999 2,371 2000 3,162 2001 1,957 2002 1,000 2003 1,468 2004 908	• Groundwater sampling

SRM Summary:

- The Toolkit SRM was used to estimate TCE groundwater concentrations in the transmissive zone following DNAPL remediation at an industrial facility. Uncertainties associated with the estimates were also evaluated. Toolkit input parameters are shown on Figure 1.2.
- The surficial sandy aquifer at the site is underlain by a thick silty aquitard. Heavy historical industrial pumping resulted in a long-term downward hydraulic gradient across the aquitard (Chapman and Parker, 2005).
- SRM "Plume Analysis" model (Section 2) was used to estimate the groundwater concentrations.
- Site hydrogeological data was entered in Section 3, transport parameters in Section 4, plume characteristics in Section 5, source loading information in Section 6, and field data for comparison in Section 7.
- Site-specific values (as documented by Chapman and Parker, 2005) were available for all parameters except "molecular diffusion coefficient in free water" and "apparent tortuosity factor exponent." For these, Toolkit default values were used.
- Since exact source concentrations were unavailable, the maximum observed concentration in the plume zone (as suggested by the Toolkit) was used as the starting point for source concentrations.
- An uncertainty of ± a factor of 10 was assumed for concentration estimations.
- A sheet pile enclosure was installed in 1994 around the DNAPL area (Figure 1.1). However, to account for the travel of contaminated groundwater present at the time of the sheet pile, an "effective" source removal time of 1996 was used in the Toolkit.
- Monitoring data from well MW-01 was used for calibration.

KEY POINTS:

The SRM of the Toolkit was able to reproduce observed groundwater concentrations to within an order of magnitude.

Use of site-specific values documented by Chapman and Parker (2005) and Toolkit default values (for 'molecular diffusion coefficient in free water' and 'apparent tortuosity factor exponent') provided a reasonable comparison to actual observed TCE concentrations in MW-01 (Figure 1.3). Therefore, no adjustment of any input parameters was necessary.

Chapman and Parker (2005) estimated a total mass in the aquitard of 3000 kg for the year 2000. Comparably, the Toolkit estimates a most likely mass of 1414 kg. This is well within the order of magnitude level of accuracy goal for this model.

Note that a typical advection-dispersion-type model would show no mass in the low-k unit, a fundamentally incorrect conceptual model. We feel using a simple model to get

within an order of magnitude to represent this difficult-to-model complex process is a significant improvement and consequently, this model provides very useful information.

Based on Toolkit SRM modeling, more than 500 years will be required for the plume to reach an MCL of 5 ug/L. This compares well to Chapman and Parker's more sophisticated modeling that indicated concentrations "will remain much above the MCL for centuries."

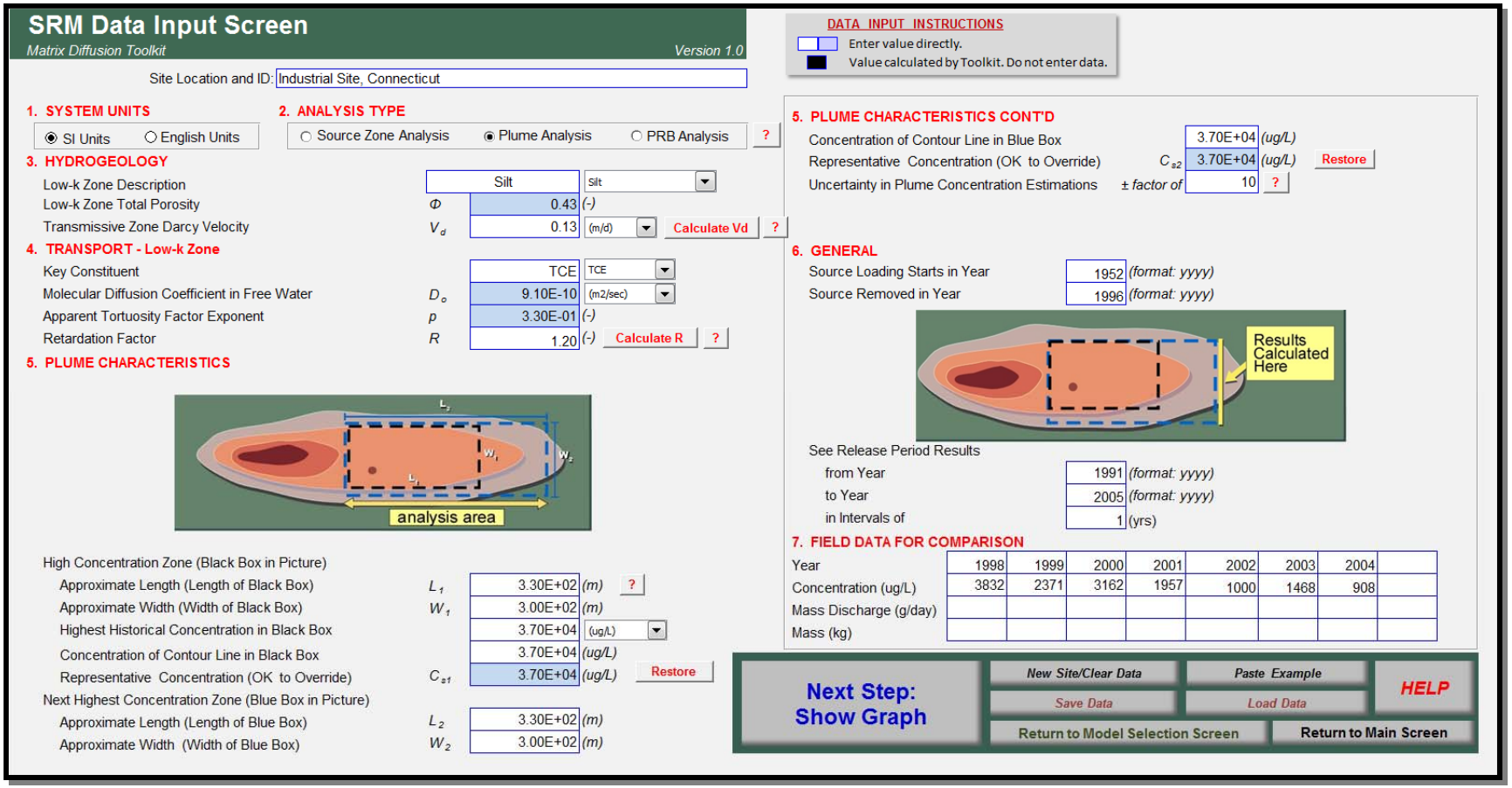

Figure 1.2. SRM Input Parameters.

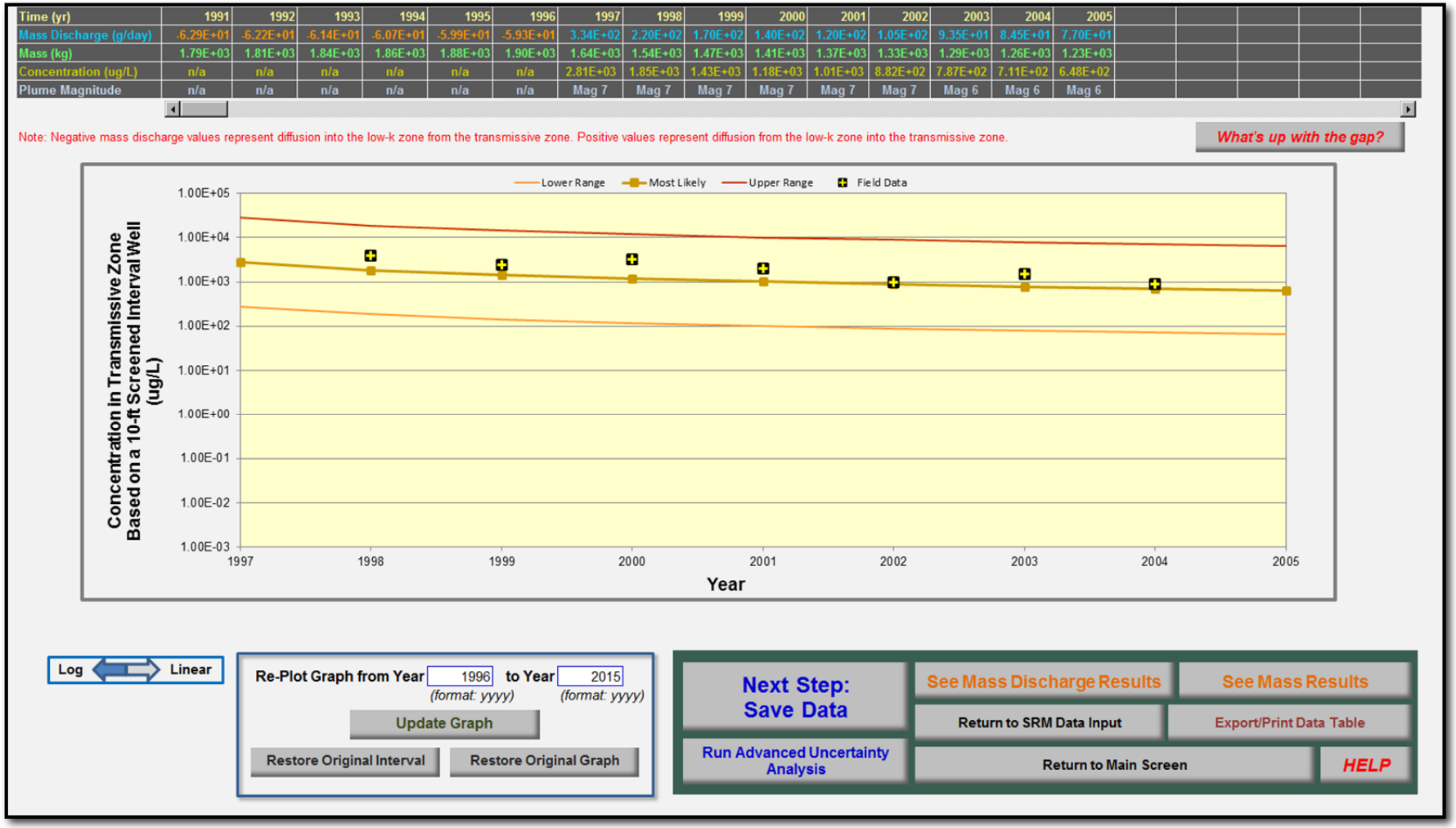

Figure 1.3. SRM Output – concentrations in the transmissive zone at location MW-01. The middle line is the most likely result from the SRM. The square symbols with crosses are actual site data. As can be seen, this results in a very close match to actual field data.

B. Dandy-Sale Model

DSM Input Data:

Data Type	Parameter	Value	Source of Data
Hydrogeology	• Trans. zone description: • Trans. zone porosity: • Low-k zone description: • Low-k zone porosity: • Trans. zone seepage velocity:	sand 0.35 (-) silt 0.43 (-) 0.37 (m/d)	• Boring logs • Site estimate • Boring logs • Site estimate • Calculated based on site estimates
Transport – Low-k Zone	• Key constituent: • Mean concentration: • Molecular diffusion coefficient in free water: • Trans. zone apparent tortuosity factor exponent: • Low-k. zone apparent tortuosity factor exponent: • Trans. zone bulk density: • Low-k zone bulk density: • Trans. zone foc: • Low-k. zone foc: • Organic carbon partitioning coefficient: • Coefficient of transverse hydrodynamic dispersion:	TCE 1100 (mg/L) 9.1E-10 (m^2/sec) 0.33 (-) 0.33 (-) 1.7 (g/mL) 1.5 (g/mL) 0.038% 0.054% 93.3 (L/kg) 0.001 (m)	• Site history • Literature TCE solubility • Literature (Toolkit default) • Literature (Toolkit default) • Literature (Toolkit default) • Site estimate • Site estimate • Site evaluation • Site evaluation • Literature (Toolkit default) • Literature (Toolkit default)
Source Zone Characteristics	• Source zone length: • Source zone width: • Source loading starts in year: • Source removed in year:	32.1 (m) 39.3 (m) 1952 source zone evaluation: 1997 plume zone evaluation: 1996 (initial) 1978 (calibrated)	• Site map • Site map • Site history • Estimated from site history
General	• See results for year: • Lateral distance from source: • Vertical depth:	1997 (source zone evaluation) 2000 (plume zone evaluation) 0.001 (m) (source zone evaluation) 280 (m) (plume zone evaluation) 3 (m)	• Site monitoring data • Site map

DSM Summary:

- The Toolkit DSM was used to estimate TCE groundwater concentrations in the low-k zone following DNAPL remediation at an industrial facility.
- The DSM was used to estimate groundwater concentrations in the low-k zone in both the source and plume areas.
- Toolkit input and output for the source zone analysis are shown on Figures 1.4 and 1.5. A comparison of the Toolkit output with observed values is shown on Figure 1.6.
- Toolkit input and output for the plume zone analysis are shown on Figures 1.7 through 1.11. A comparison of the Toolkit output with observed values is shown on Figure 1.12.
- Site hydrogeological data was entered in Section 2, transport parameters in Section 3, source zone characteristics in Section 4, and desired output information in Section 5.
- Site-specific values (as documented by Chapman and Parker, 2005) were available for all parameters except "molecular diffusion coefficient in free water", "apparent tortuosity factor exponent," "organic carbon partitioning coefficient", and "coefficient of transverse hydrodynamic coefficient." For these, Toolkit default values were used. Additionally, the Toolkit default value for the organic carbon partitioning coefficient was also used.
- A sheet pile enclosure was installed in 1994 around the DNAPL area (Figure 1.1).
    - For the source zone analysis, field comparison data were collected *inside* the sheet pile enclosure in 1997, therefore, for this analysis the source was assumed to be active in 1997.
    - For the plume zone analysis, to account for the travel of contaminated groundwater present at the time of the sheet pile, an "effective" source removal time of 1996 was used initially in the Toolkit. However, the exact history of the source concentration is unknown, therefore this parameter was used as a calibration parameter. Specifically, initially, the source concentration was assumed to be constant at 475 mg/L (average of the estimated vs. time curve from Chapman and Parker (2005)) for 44 years and then turned off (Figures 1.7, 1.8, and 1.12). During the calibration process, the solubility limit of TCE was used as the concentration and this time period was adjusted to better match the observed concentrations at location ML-10 in the year 2000 (Figures 1.9, 1.10, 1.11, and 1.12).
- Monitoring data from the low-k zone at locations WCP-70 and WCP-71 inside the sheet pile enclosure and location ML-10 were used for comparison to simulated source and plume concentrations, respectively.

KEY POINTS:

The DSM of the Toolkit was able to reproduce observed groundwater concentrations within an order of magnitude.

Use of site-specific values documented by Chapman and Parker (2005) and Toolkit default values for parameters with no site-specific information provided a reasonable comparison to actual observed TCE concentrations in the source zone (Figure 1.6). Therefore, no adjustment of any input parameters was necessary. A comparison using the observed reported maximum source concentration of 1300 mg/L also yielded a reasonable comparison without any input parameter value adjustments.

To determine how closely the Toolkit could match a declining source, we took the estimated vs. time curve from Chapman and Parker (2005) and assumed an average constant concentration of 475 mg/L for 42 yrs. However, this did not show a good comparison with the observed concentrations. A better match was obtained by assuming a constant 1100 mg/L source active for 26 years (Figure 1.9). Note that although only the source concentration and year in which the source was removed were used as calibration parameters for this evaluation, other combinations of input parameters could be adjusted to yield similar results. This shows that having actual data available for calibration improves the overall simulation results.

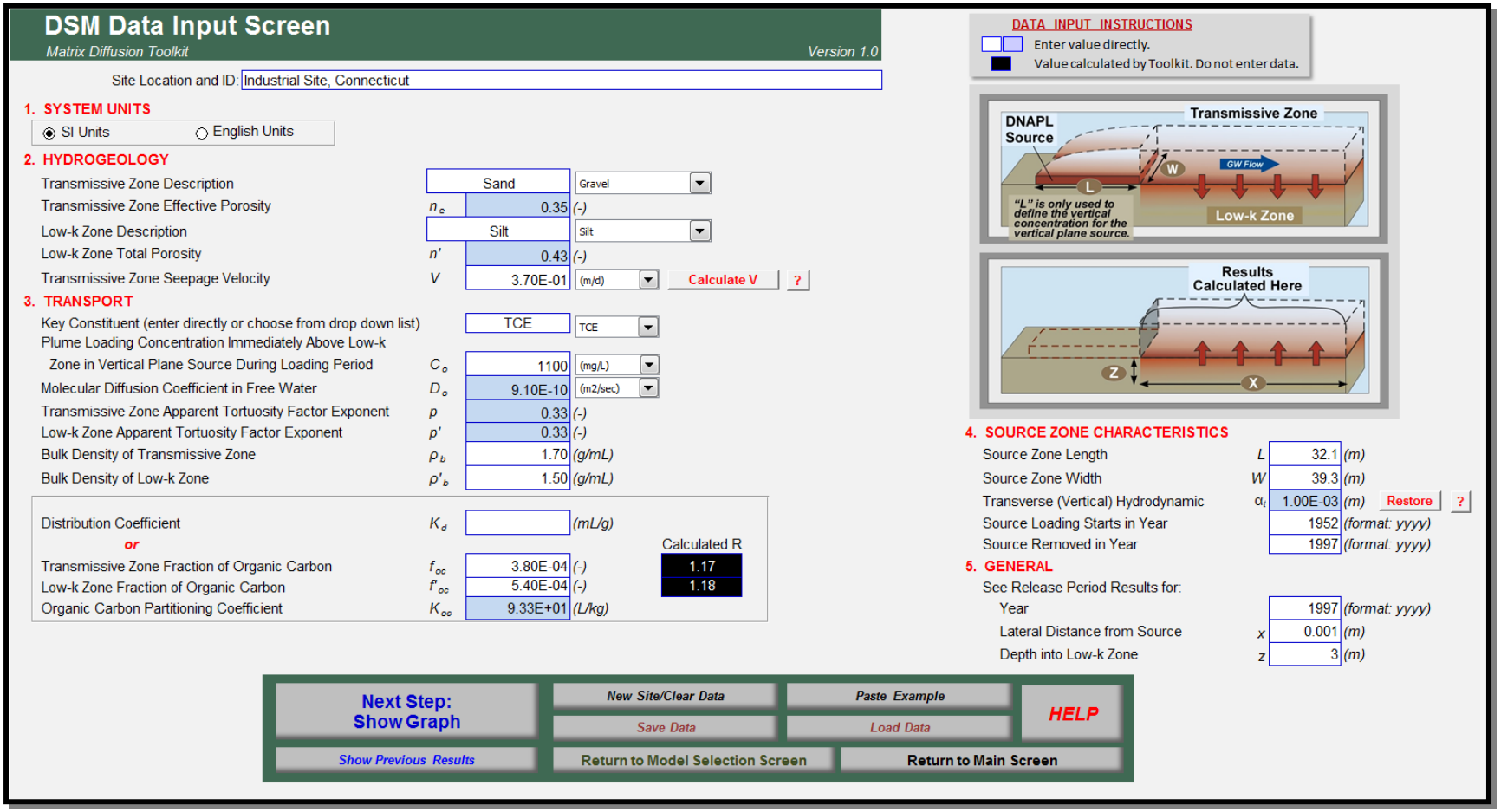

Figure 1.4. DSM Input Parameters – Source Zone Evaluation.

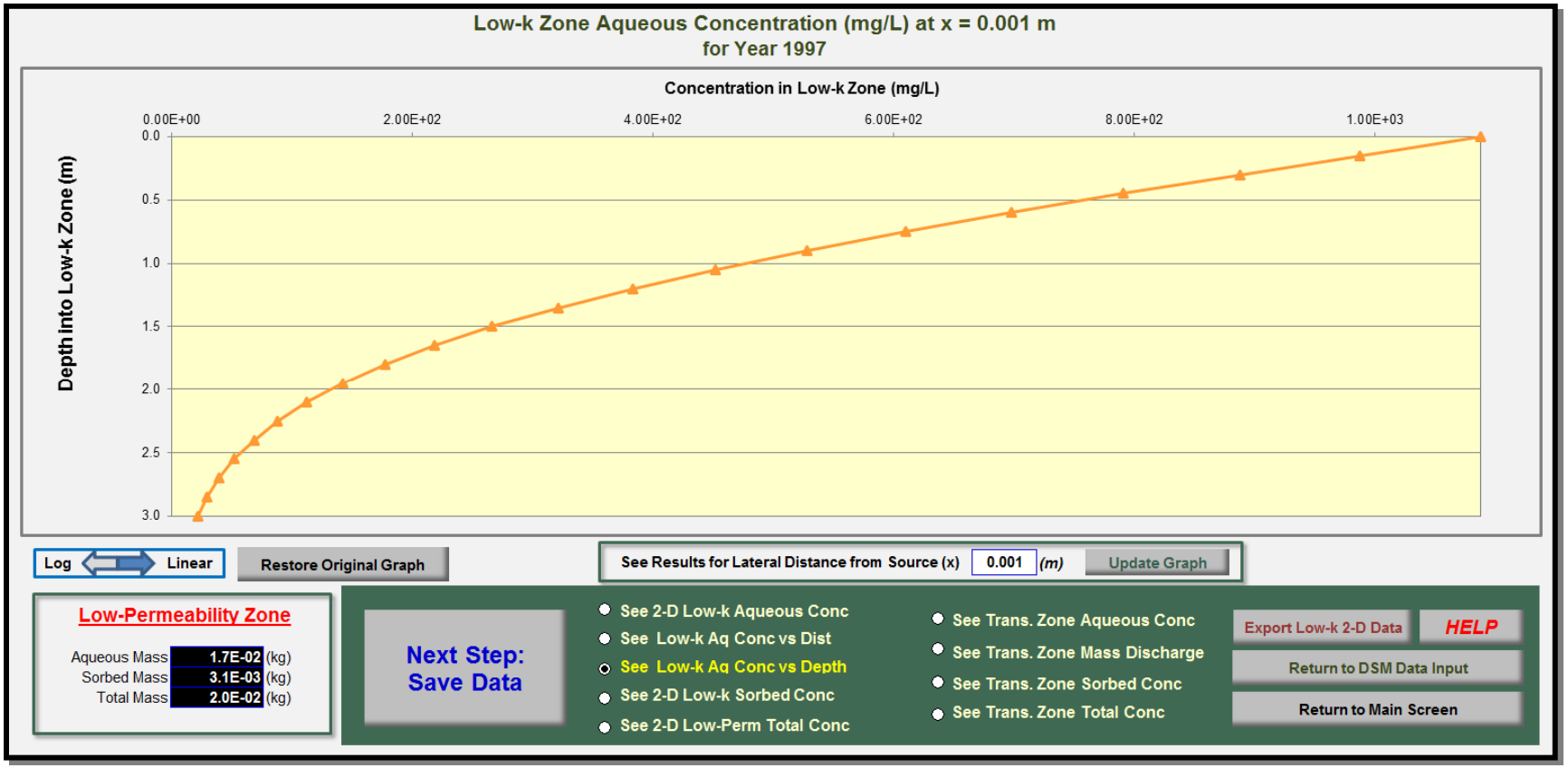

Figure 1.5. DSM Output – Source Area Low-k Zone Concentrations.

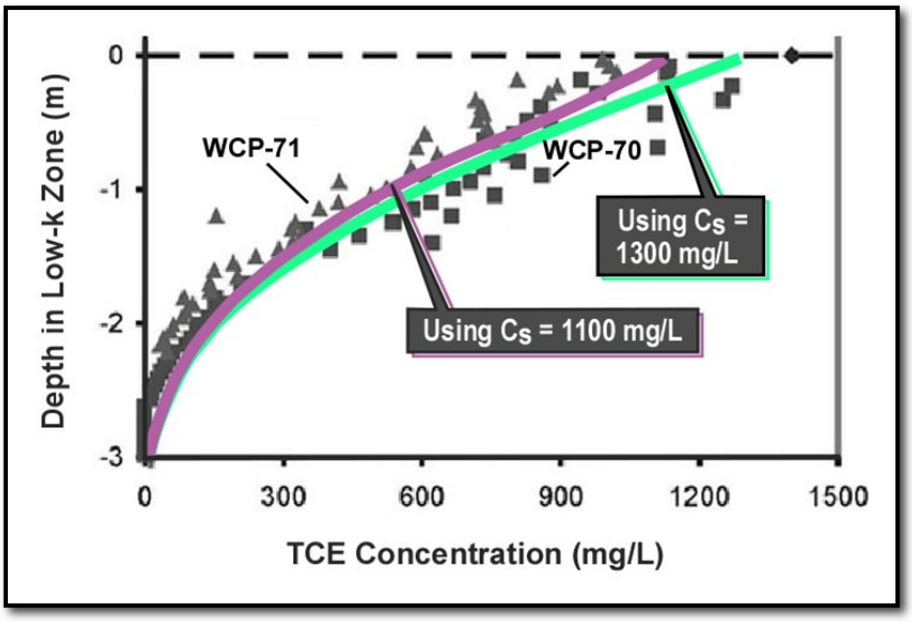

Figure 1.6. Comparison of DSM Source Area Low-k Concentrations (Green and Purple Lines) against Observed Concentrations in WCP-70 and WCP-71 in 1997. Based on Figure 6a of Chapman and Parker (2005). The match between actual and modeled results is very close.

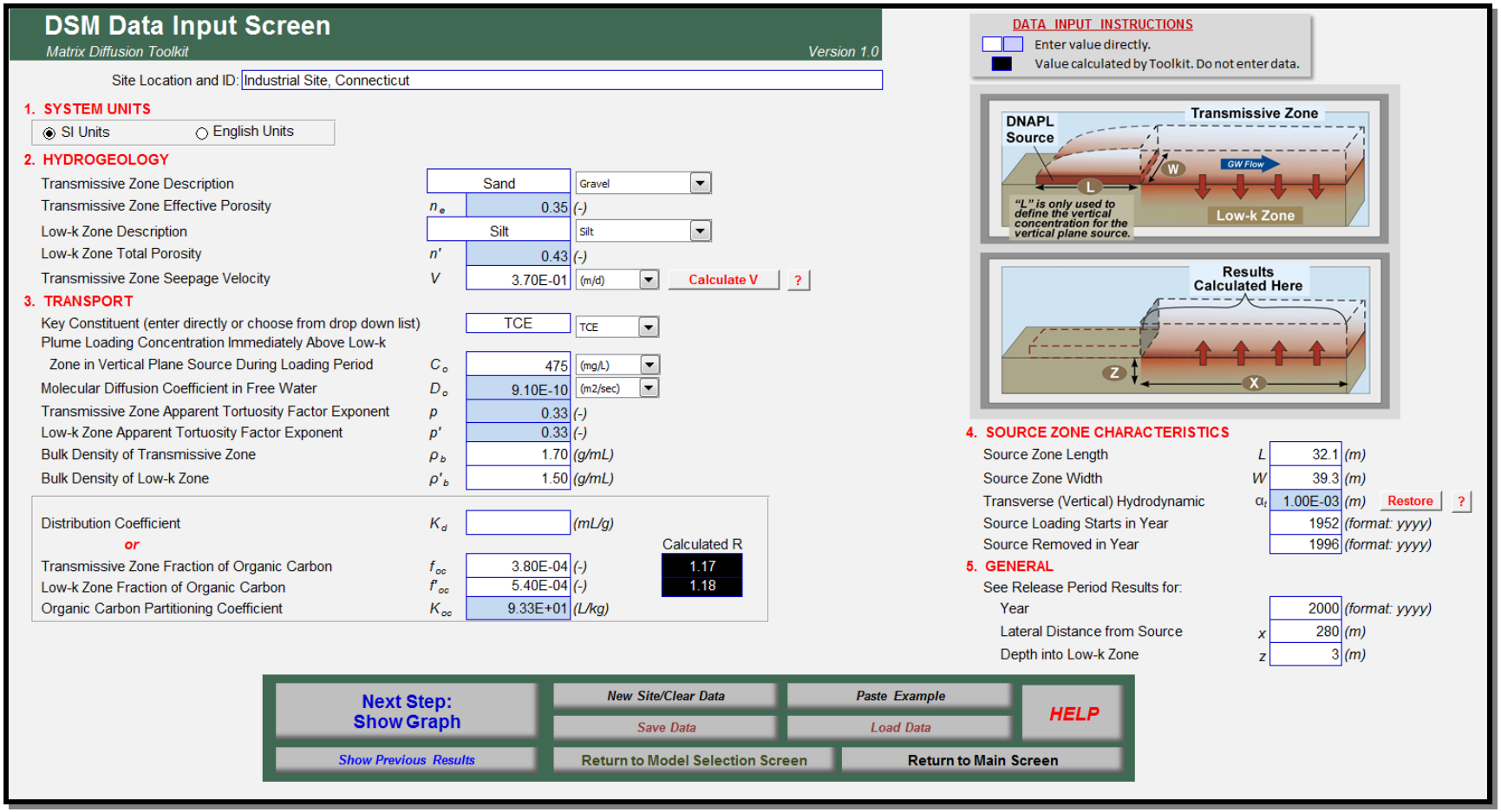

Figure 1.7. DSM Input Parameters – Plume Zone Evaluation (Initial).

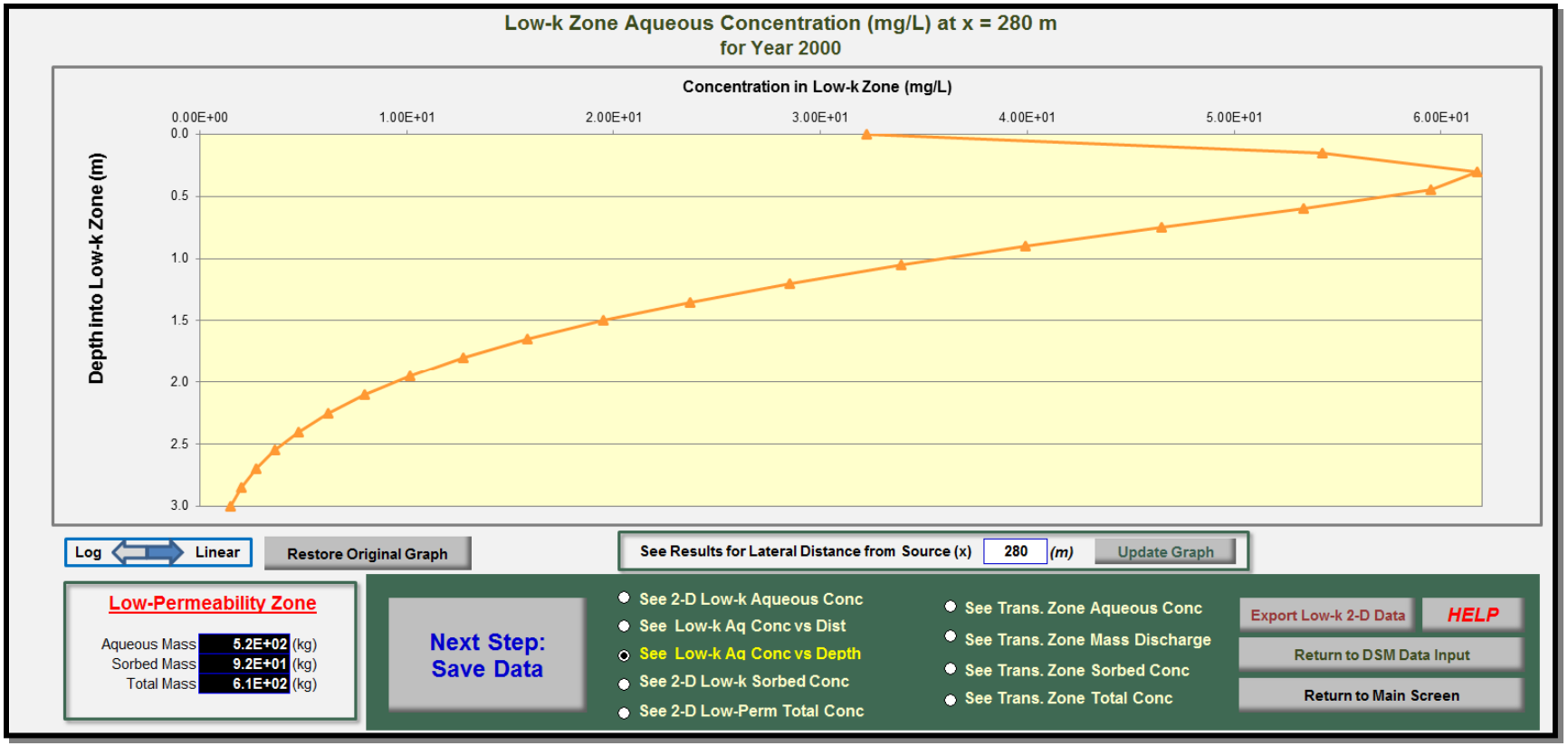

Figure 1.8. DSM Output – Plume Area Low-k Zone Concentrations (Initial).

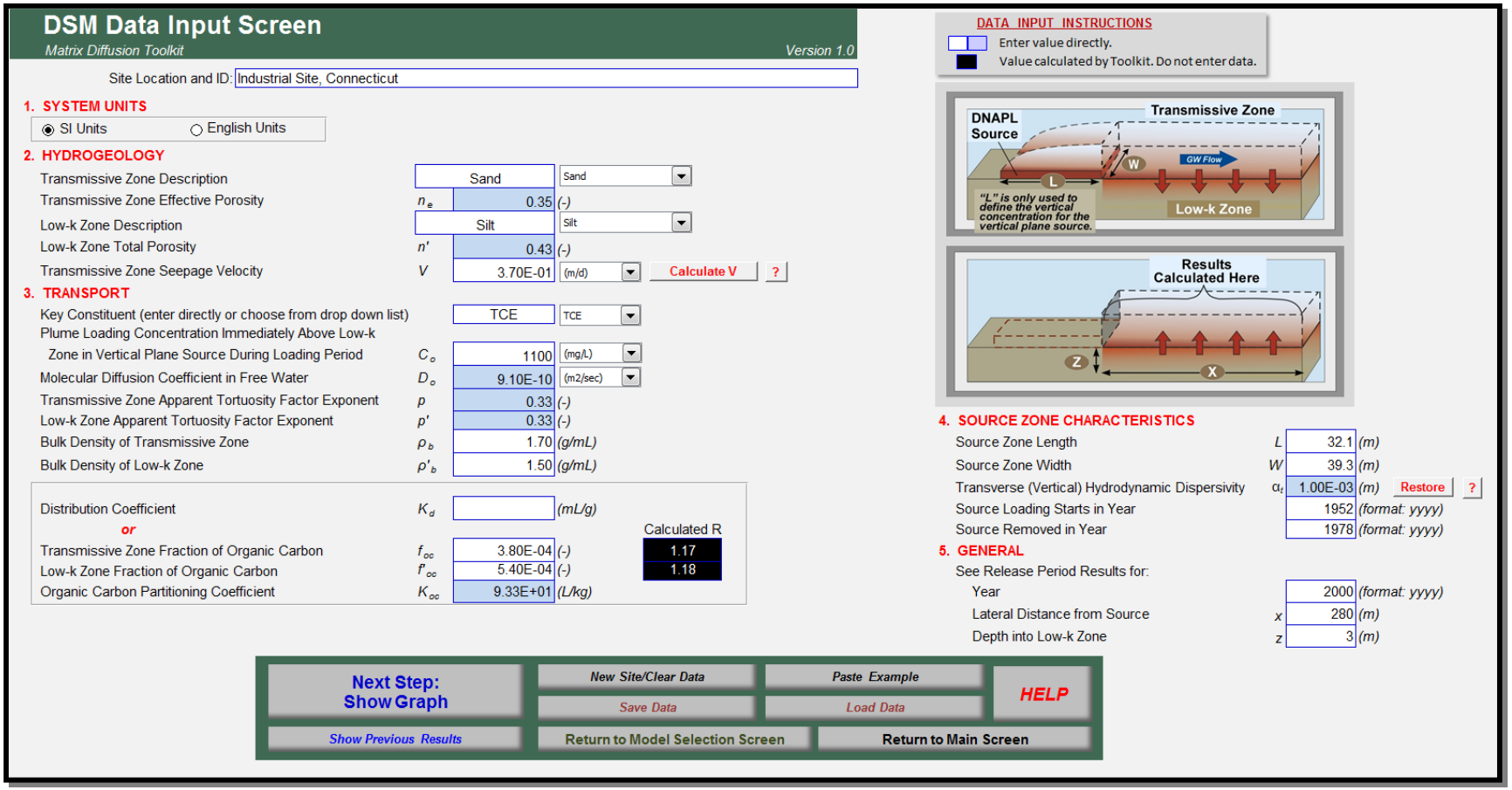

Figure 1.9. DSM Input Parameters – Plume Zone Evaluation (Calibrated).

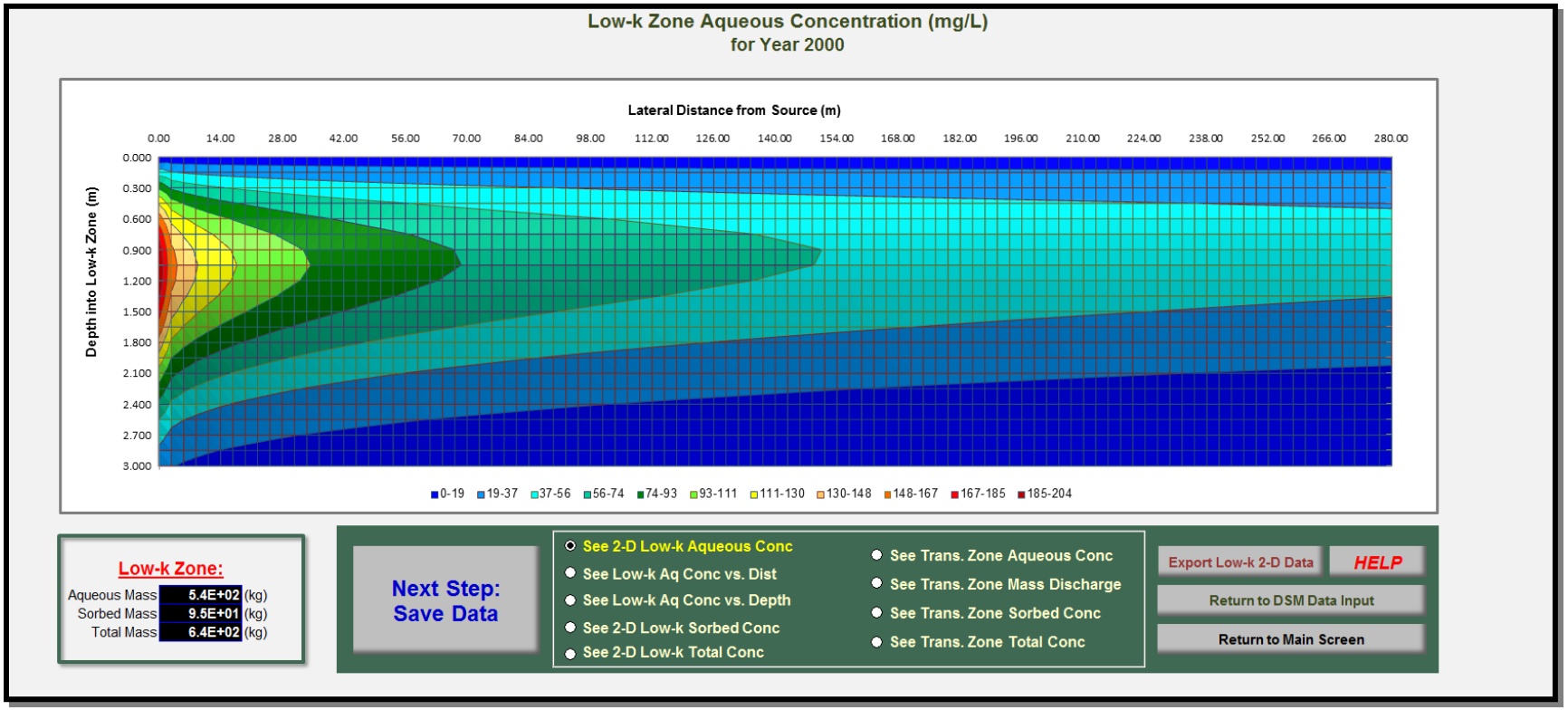

Figure 1.10. DSM Output – Plume Area Low-k Zone Concentrations (Calibrated).

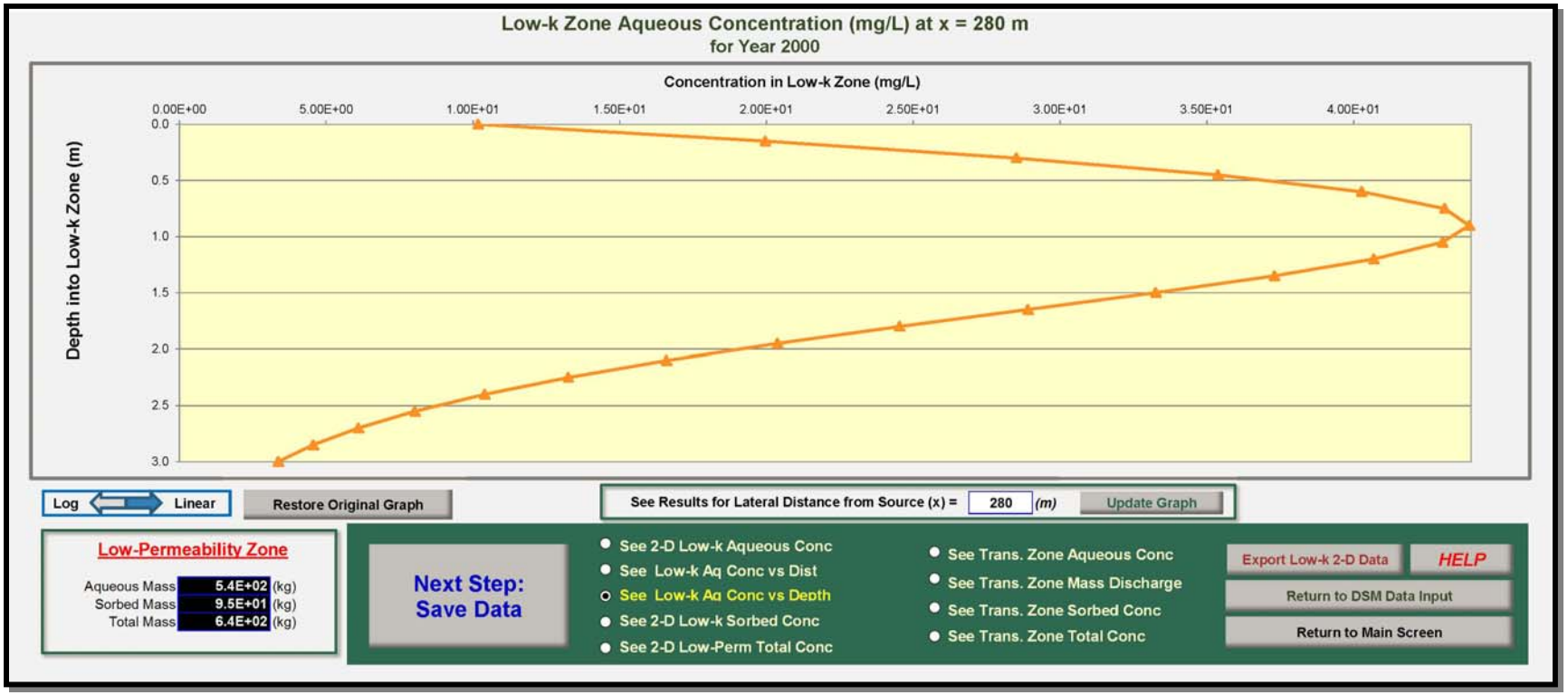

Figure 1.11. DSM Output – Plume Area Low-k Zone Concentrations (Calibrated).

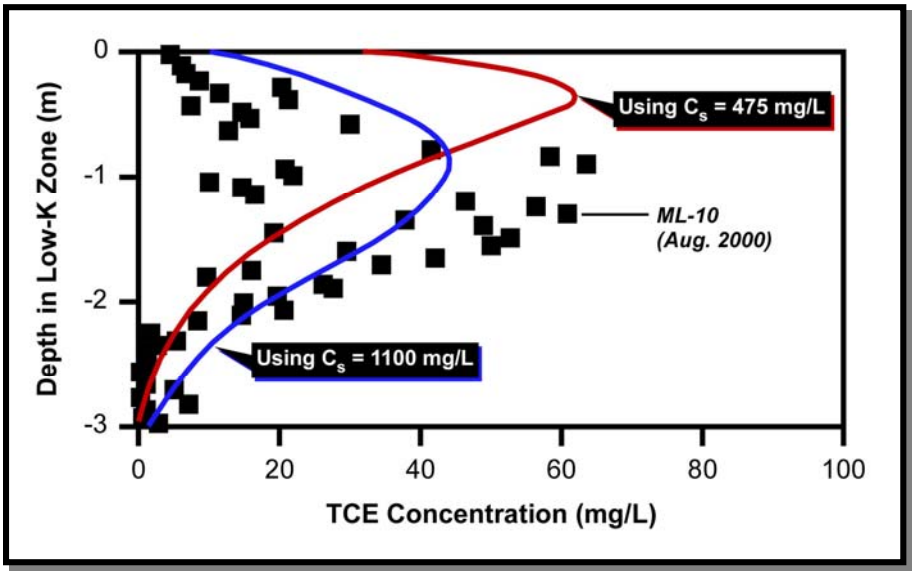

Figure 1.12. Comparison of DSM Plume Area Low-k Concentrations (Red and Blue Lines) with Observed Concentrations in ML-10 in 2000. Based on Figure 6b of Chapman and Parker (2005). The calibrated value (C_s = 1100 mg/L loading concentration for first 26 years) resulted in a better match to actual site data than the original estimate of loading concentration (475 mg/L over 42 years).

CASE STUDY 2. SAND TANK STUDY

Overview:

The Toolkit was used to estimate the effects of diffusion into and from low-k zones for tracers (bromide and fluorescein) in a sand tank. The sand tank study is described in detail in Chapman *et al*. (2012).

For this analysis, both the SRM (Case Study 2A) and the DSM (Case Study 2B) were applied as follows:

- Step 1: Initial values of all parameters, obtained from either Chapman *et al*. (2012) or default Toolkit parameters, were entered into the Toolkit.
- Step 2. Toolkit outputs were compared to observed tracer concentrations. This step was critical in determining how well Toolkit default parameters predicted actual field conditions.
- Step 3. Input parameters were adjusted, as needed, to improve the comparison with observed tracer concentrations.

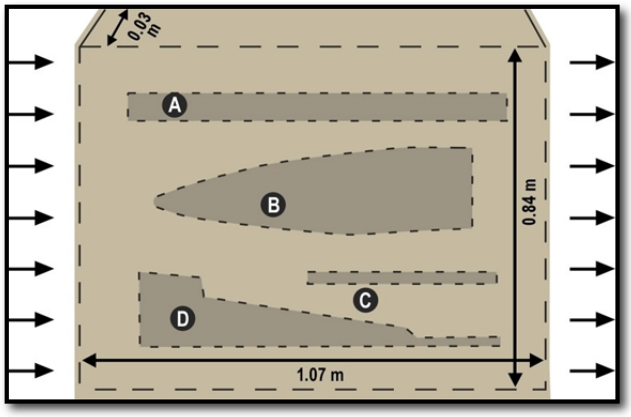

Figure 2.1. Sand Tank Configuration. Based on Chapman *et al*. (2012) Figure 1. Darker shaded areas (A, B, C, and D) represent low-k bentonite zones lying in transmissive sandy zones.

A. Square Root Model

SRM Input Data:

Data Type	Parameter	Value	Source of Data
Hydrogeology	• Low-k zone description: • Low-k zone porosity: • Darcy velocity:	clay 0.60 (-) 1.51E-4 (cm/sec)	• Sand tank construction • Estimated (sand tank study) • Experimental (sand tank study)
Transport – Low-k Zone	• Key constituent: • Molecular diffusion coefficient in free water: • Apparent tortuosity factor exponent: • Retardation factor:	bromide; fluorescein bromide: 2.01E-9 (m^2/sec) fluorescein: 5.5E-10 (m^2/sec) 1 (-) 1 (-)	• Sand tank • Literature (sand tank study) • Literature (sand tank study) • Assumed (sand tank study)
Plume Characteristics	• High concentration zone • Approximate length: • Approximate width: • Highest concentration in black box: • Concentration of contour line in black box: • Representative concentration: • Next highest concentration zone • Approximate length: • Approximate width: • Concentration of contour line in blue box: • Representative concentration: • Uncertainty in plume concentration estimations:	 0.71 (m) 0.03 (m) 1 (mg/L) 1 (mg/L) Initial: 1 (mg/L) Calibrated: 1.88 (mg/L) (fluorescein) 0.71 (m) 0.03 (m) 1 (mg/L) Initial: 1 (mg/L) Calibrated: 1.88 (mg/L) (fluorescein) 10 (± factor of)	• Based on area of lengths of clay layers in sand tank and width of tank
General	• Source loading starts in year: • Source removed in year:	2006 24 days	• Sand tank study • Sand tank study
Field Data for Comparison	• Effluent bromide and fluorescein concentrations		• See Figures 2.4 and 2.7

SRM Summary:

- The Toolkit SRM was used to estimate bromide and fluorescein tracer groundwater effluent concentrations from a sand tank. For fluorescein, input parameters are shown on Figures 2.2 and 2.3 and comparisons of simulated and observed concentrations on Figure 2.4. For bromide, input parameters are shown on Figure 2.5 and output on Figure 2.6.
- SRM "Plume Analysis" model (Section 2) was used to estimate the groundwater concentrations.
- Site hydrogeological data was entered in Section 3, transport parameters in Section 4, plume characteristics in Section 5, and source loading information in Section 6.
- Site-specific values (as documented by Chapman *et al*. (2012)) were used for all parameters.
- An uncertainty of ± a factor of 10 was assumed for concentration estimations.
- To account for the flushing time in the tank, model output from Day 25 (the end of the loading period) were compared to tank data from Day 32 (the end of the loading plus 7 days of flushing of the transmissive zone). This allowed for a pure diffusion vs. diffusion comparison between model and tank data.
- Monitoring data from the sand tank study was used for calibration.
- The SRM assumes diffusion into and from the top interface of a single low-k layer. To account for the four distinct clay layers and associated eight interfaces in the sand tank, the SRM output concentrations were multiplied by eight.
- Note that the Toolkit has a built in 1-yr transition period between diffusion into the matrix and release from the matrix. Because the total experiment time of 120 days is less than 1-yr, this transition time was temporarily changed to 1-day for this Case Study.

KEY POINTS:

The purpose of this evaluation was to determine if the SRM in the Toolkit could be applied to simulate a difficult problem: four very thin layers in a system with advection. As described in the "Uses and Limitations" Section (page 4), the SRM model assumes a two-layer system with one interface, an infinitely thick low-k zone, and instantaneous flushing of the transmissive zone (instantly changing from the loading period to the release period). The tank study had four very thin low-k zones ranging from 0.03 to 0.2 meters thick compared to a theoretical contaminant penetration depth into an infinite low-k zone of 0.25 m. Finally, the tank had a relatively long flushing period (7 days compared to the total experiment time of 120 days). Despite these differences from the assumed configuration of the SRM, the end results show the model was able to match the actual data from the tank within an order of magnitude.

For fluorescein, although the general shape of the observed concentrations was followed, using tank-specific values documented by Chapman *et al.* (2012), simulated concentrations were consistently underestimated by about a factor of 3. A much better

fluorescein comparison of simulated and observed concentrations was obtained by using the maximum observed concentration as the source concentration. For bromide, concentrations were underestimated closer to the source cut-off and overestimated towards the end of the simulations.

Although there are various combinations of input parameters could be varied to improve the comparison of simulated and observed concentrations, for this analysis, the parameter adjusted was the loading concentration. Increasing the loading concentration yielded a close match to the observed fluorescein concentration vs. time data.

These results show that the Square Root Model can simulate complex heterogeneous systems that don't meet all of the assumptions, and still provide useful simulation results that are within an order of magnitude.

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References

Chapman S.W. and B.L. Parker, T.C. Sale, and L. A. Doner, 2012. Testing high resolution numerical models for analysis of contaminant storage and release from low permeability zones, *J. Cont.* Hydrology 136–137: 106–116.

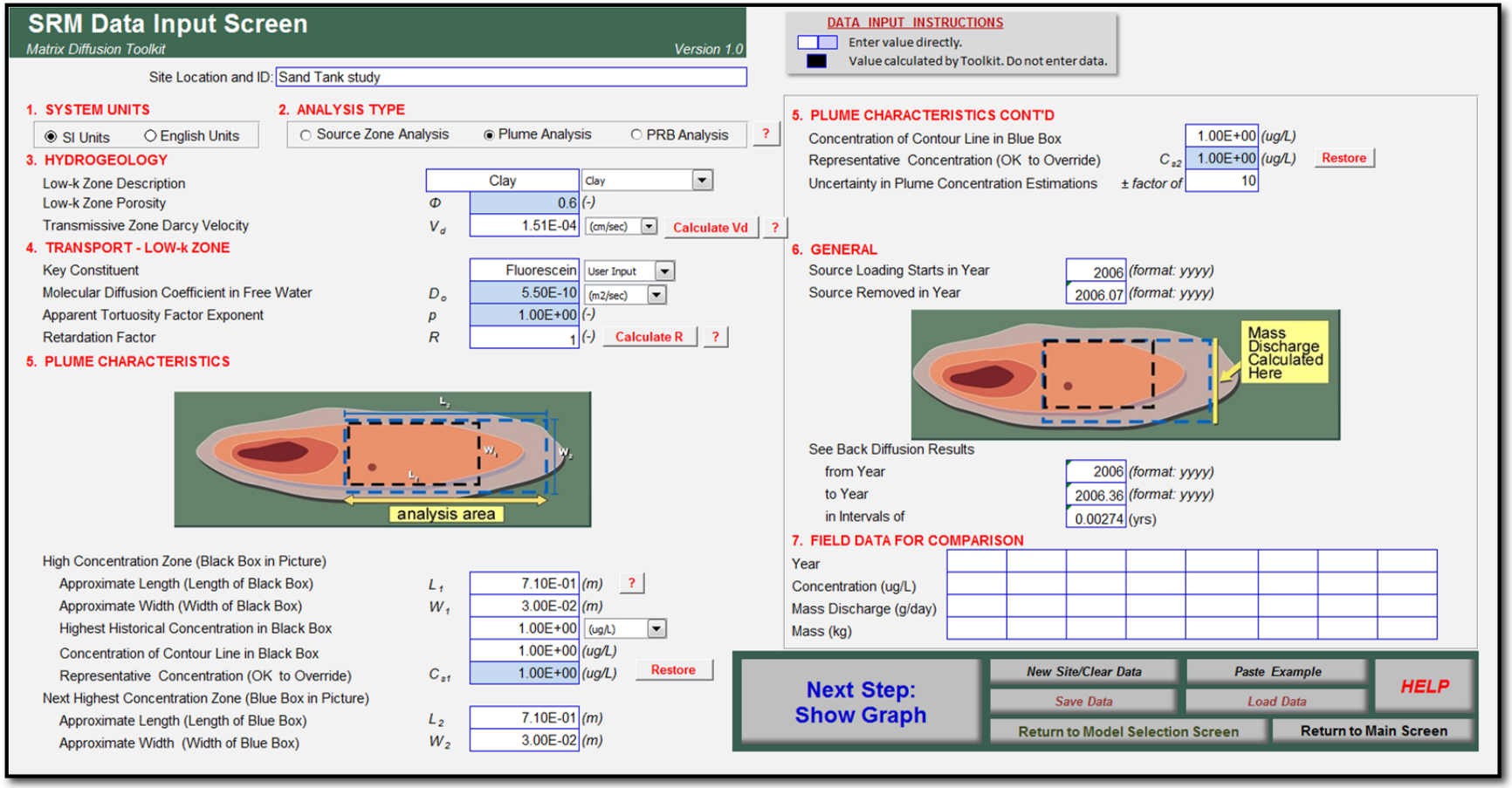

Figure 2.2. SRM Input Parameters – Fluorescein (Initial).

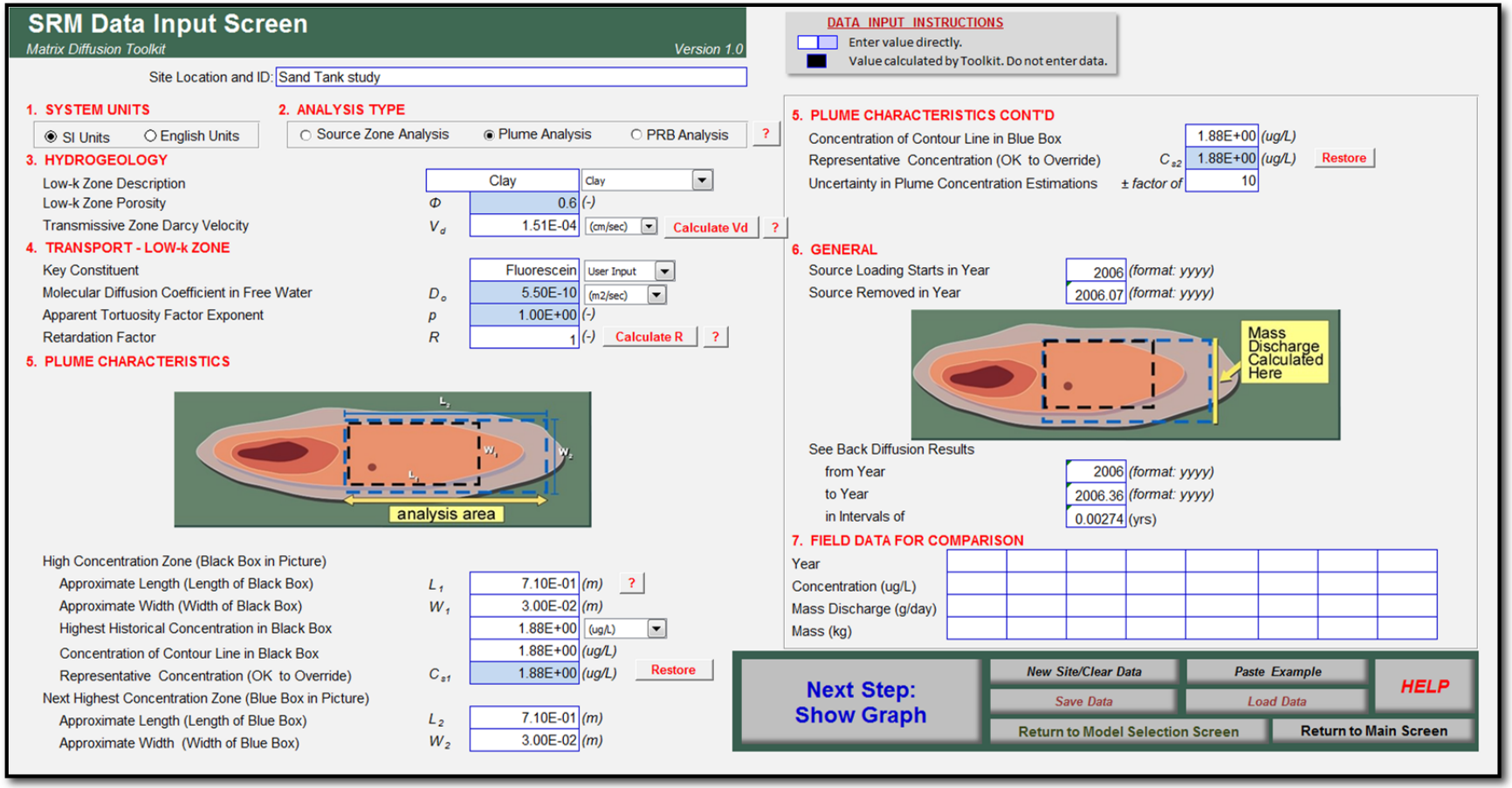

Figure 2.3. SRM Input Parameters – Fluorescein (Calibrated. Source concentration changed to 1.88 mg/L).

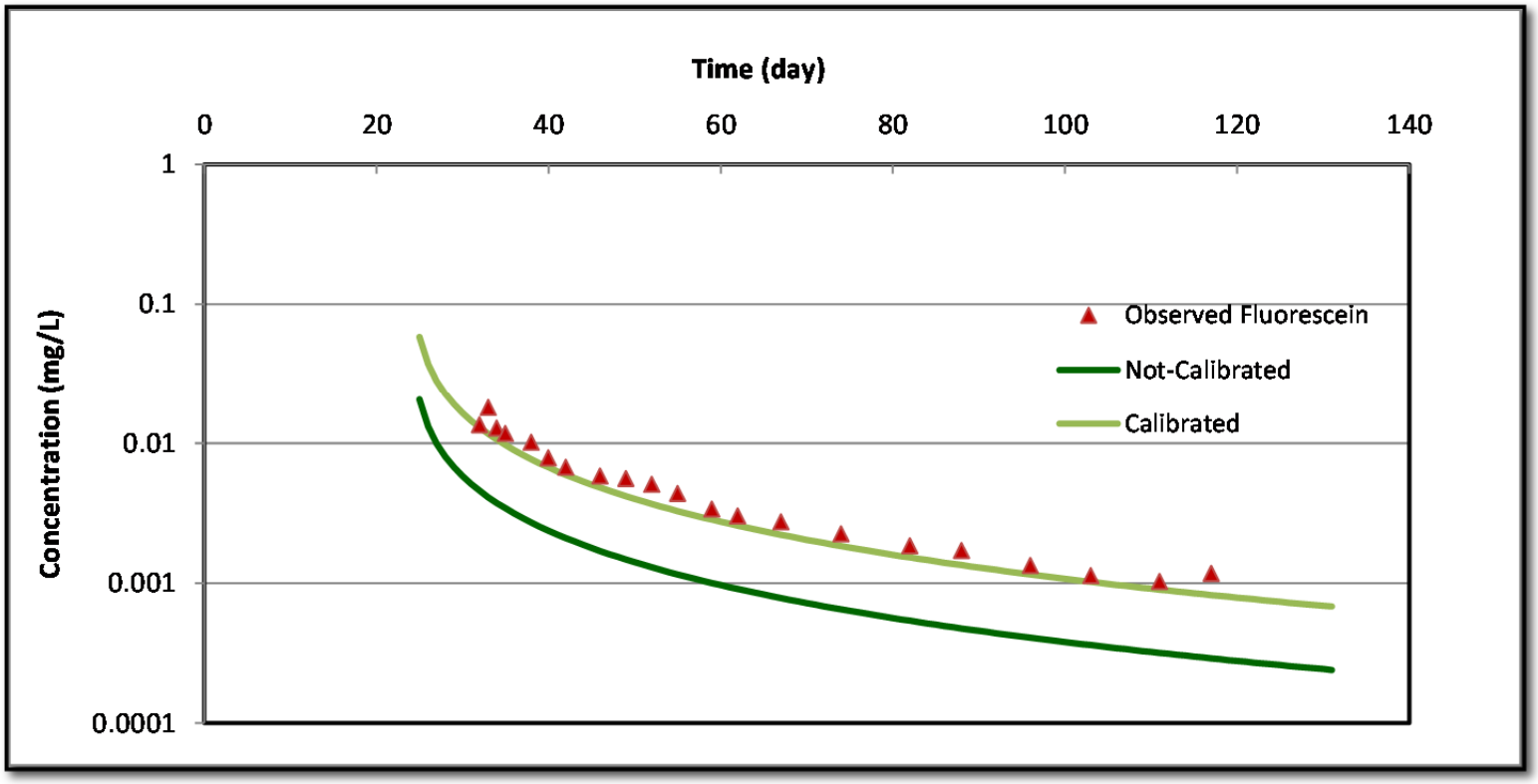

Figure 2.4. Comparison of SRM (Green Lines) against Observed Concentrations - Fluorescein. The dark green line represents output using initial parameters. The light green line represents the calibrated model output. The overall shape of the uncalibrated model result matched the data and was within one order of magnitude. The calibrated model was a very close match to experimental data.

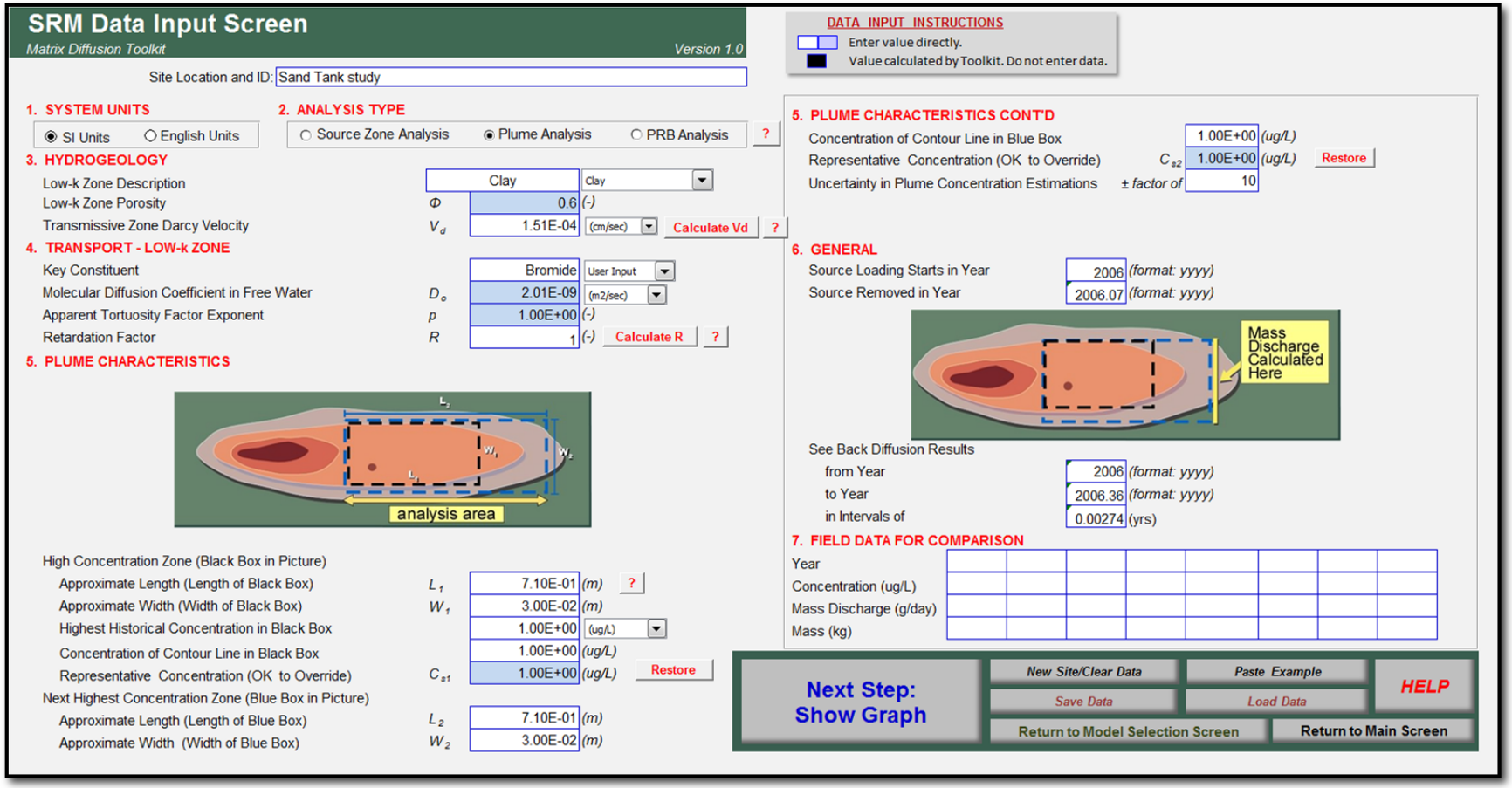

Figure 2.5. SRM Input Parameters – Bromide.

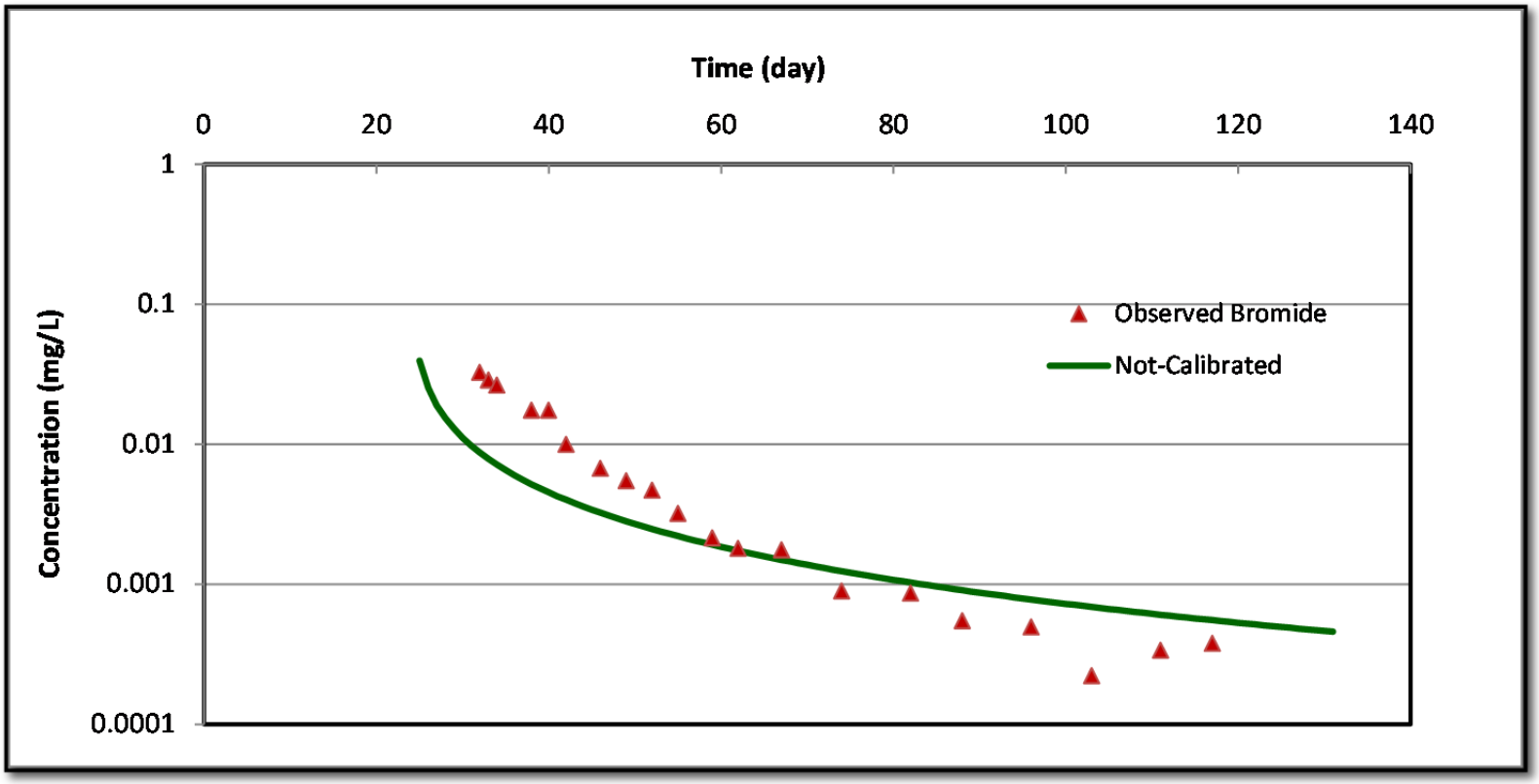

Figure 2.6. Comparison of SRM (Green Lines) against Observed Concentrations - Bromide. The dark green line represents output using initial parameters. The light green line represents the calibrated comparison. Although visually not as good a match as the fluorescein data, the overall trend in the data matched within an order of magnitude.

B. Dandy-Sale Model

DSM Input Data:

Data Type	Parameter	Value	Source of Data
Hydrogeology	• Trans. zone description: • Trans. zone effective porosity: • Low-k zone description: • Low-k zone porosity: • Trans. zone seepage velocity:	sand 0.45 (-) clay 0.60 (-) 3.36E-4 (cm/sec)	• Sand tank construction • Sand tank construction • Sand tank construction • Estimated (sand tank study) • Experimental (sand tank study)
Transport – Low-k Zone	• Key constituent: • Mean concentration: • Molecular diffusion coefficient in free water: • Trans. zone apparent tortuosity factor exponent: • Low-k. zone apparent tortuosity factor exponent: • Trans. zone bulk density: • Low-k zone bulk density: • Retardation factor: • Organic carbon partitioning coefficient: • Transverse (Vertical) hydrodynamic dispersivity:	fluorescein 1 (mg/L) 5.5E-10 (m^2/sec) 1 (-) 1 (-) 1.7 (g/mL) 1.7 (g/mL) 1 93.3 (L/kg) 0.001 (m)	• Sand tank • Sand tank • Literature (sand tank study) • Literature (sand tank study) • Literature (sand tank study) • Literature (Toolkit default) • Literature (Toolkit default) • Literature (sand tank study) • Literature • Literature (Toolkit default)
Source Zone Characteristics	• Source zone length: • Source zone width: • Source loading starts in year: • Source removed in year:	10000 (m) 0.03 (m) 2006 24 days	• Assumed to account for the extremely thin clay layers • Based on area of lengths of clay layers in sand tank and width of tank
General	• See results for year: • Lateral distance from source: • Vertical depth:	30, 62, 89, 124 days 0.71 (m) 0.001 (m)	• Sand tank study • Sand tank study • Sand tank study

DSM Summary:

- The Toolkit DSM was used to estimate fluorescein groundwater concentrations in the low-k zone in a sand tank.
- Toolkit inputs are shown on Figure 2.7. The un-calibrated parameter set was used for this analysis.
- Hydrogeological data was entered in Section 2, transport parameters in Section 3, source zone characteristics in Section 4, and desired output information in Section 5.
- Site-specific values (as documented by Chapman *et al*., 2012) were available for all parameters except bulk densities, "organic carbon partitioning coefficient" and "Transverse (Vertical) Hydrodynamic Dispersivity." For these, Toolkit default/literature values were used. Values of zero were used to calculate retardation factors of one.
- To account for the travel of contaminated groundwater present at the time of the source removal, an "effective" source removal time of 24 days was used in the Toolkit.
- Transmissive zone concentrations output from the Toolkit were multiplied by eight (to account for the eight interfaces of the four clay layers) and 2.96 (adjusted for the height of the tank compared to the Toolkit built-in 10-ft well screen). Comparison of the observed and simulated concentrations is provided below:

	Simulation Time (days)			
	30	**62**	**89**	**124**
Observed Concentration (mg/L)	0.076	0.0044	0.0018	0.0012
Simulated Concentration (mg/L)	0.031	0.0036	0.0018	0.0010
Simulated/Observed	0.40	0.82	0.97	0.85

KEY POINT:

The purpose of this evaluation was to see if the Toolkit DSM could simulate a difficult problem: four very thin layers in a system with advection. As described in the "Uses and Limitations" section (page 4), the DSM model assumes a two-layer system with one interface, an infinitely thick low k zone, and instantaneous flushing of the transmissive zone (instantly changing from the loading period to the release period). The tank experiment had four very thin low-k zones ranging from 0.03 to 0.2 m thick compared to a theoretical contaminant penetration depth into an infinite low-k zone of 0.25 m. Despite these differences from the assumed configuration of the DSM, end results show the model was able to match actual data from the tank within an order of magnitude.

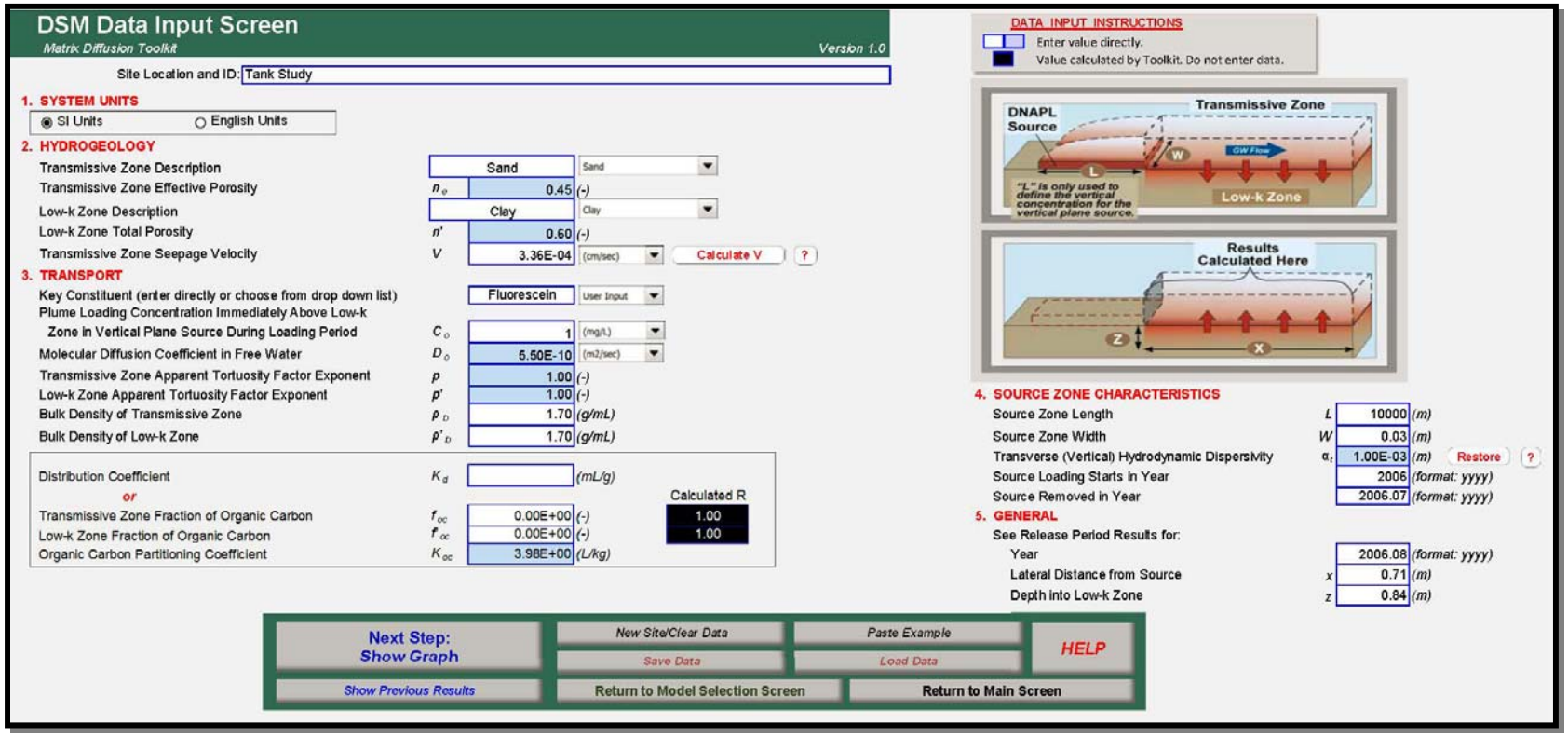

Figure 2.7. DSM Input Parameters – Fluorescein (shown for output time 30 days).

CASE STUDY 3. FORMER DRY CLEANER, FLORIDA

Overview:

The Toolkit was used to estimate the effects of diffusion into and from low-k zones at the former Building 106 area in Operable Unit 3 (OU3), a former dry cleaner site, at Naval Air Station (NAS) Jacksonville, Florida studied by GSI Environmental and the University of Guelph. The site was studied using University of Guelph high-resolution core sampling techniques. Mr. Mike Singletary of the Naval Facilities Engineering Command was the Navy point of contact for this project.

The DSM was used for this analysis and applied as follows:

- Step 1: Due to a lack of historical information on the site, Toolkit default values were used as initial parameters.
- Step 2. Toolkit outputs were compared to observed tetrachloroethene (PCE) soil concentrations at three locations in the downgradient plume.
- Step 3. Input parameters were adjusted, as needed, to improve the comparison of simulated and observed PCE concentrations.

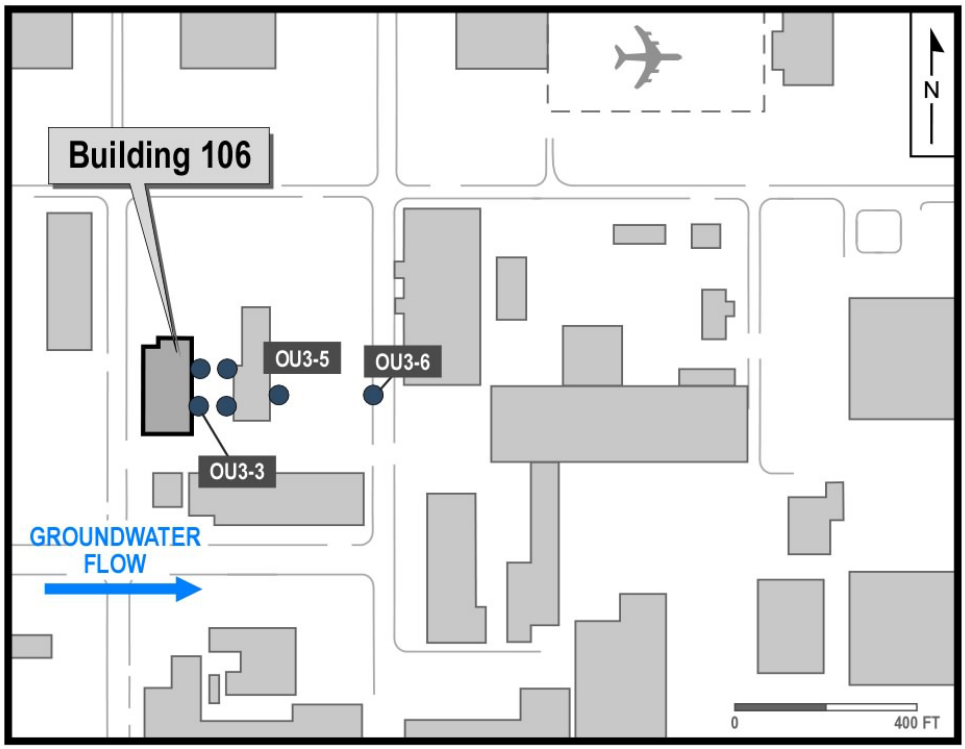

Figure 3.1. Site Layout. Building 106 in Operable Unit 3, Naval Air Station, Jacksonville, Florida.

DSM Input Data:

Data Type	Parameter	Value	Source of Data
Hydrogeology	• Trans. zone description: • Trans. zone porosity: • Low-k zone description: • Low-k zone porosity: • Trans. zone seepage velocity:	sand 0.25 (-) clay 0.47 (-) Initial: 20 (ft/yr) Calibrated: 25 (ft/yr)	• Site information • Literature (Toolkit default) • Site information • Literature (Toolkit default) • Estimated site information
Transport – Low-k Zone	• Key constituent: • Mean concentration: • Molecular diffusion coefficient in free water: • Trans. zone apparent tortuosity factor exponent: • Low-k. zone apparent tortuosity factor exponent: • Trans. zone bulk density: • Low-k zone bulk density: • Trans. zone fraction organic carbon: • Low-k. zone fraction organic carbon: • Organic carbon partitioning coefficient: • Coefficient of transverse hydrodynamic dispersion:	PCE Initial: 60 (mg/L) Calibrated: 143 (mg/L) Initial: 8.2E-10 (m^2/sec) Calibrated: 4.2E-10 (m2/sec) 0.33 (-) 1.33 (-) 1.7 (g/mL) 1.7 (g/mL) 0.05% Initial: 0.1% Calibrated: 0.15% 155 (L/kg) 0.0003 (ft)	• Site information • Initial - maximum observed • Calibrated (PCE solubility) • Literature (Toolkit default). Calibrated value within the range of values reported in literature • Literature (Toolkit default) • Literature (Toolkit default) • Literature (Toolkit default) • Literature (Toolkit default) • Estimated site information • Estimated site information Calibrated – within range of estimated site values • Literature (Toolkit default) • Literature (Toolkit default)
Source Zone Characteristics	• Source zone length: • Source zone width: • Source loading starts in year: • Source removed in year:	56 (ft) 102 (ft) 1962 2011	• Estimated as 50% of building length. • Estimated as 50% of building width. • Estimated site information • Assumed continuous source
General	• See results for year: • Lateral distance from source: • Vertical depth:	2011 65 (ft) 16.5 (ft)	• Field data • Site map (distance of OU3-3 from the source) • Field data

DSM Summary:

- The Toolkit DSM was used to estimate PCE soil concentrations in the low-k zone at a former dry cleaner site (OU-3 Building 106) at Naval Air Station Jacksonville, Florida studied using University of Guelph high-resolution core sampling techniques. Mr. Mike Singletary of the Naval Facilities Engineering Command was the point of contact for this project.
- Due to availability of limited site information, Toolkit default values were used as input parameters where necessary. Seepage velocity, initial source concentration, and low-k formation fraction organic carbon were varied until a reasonable comparison between simulated and observed concentrations was obtained at the three field observation locations.
- Toolkit inputs are shown on Figures 3.2 and 3.3 for the initial and calibrated models, respectively. A DSM output is shown on Figure 3.4, while comparisons of the Toolkit simulated with observed values are shown on Figures 3.4, 3.5, and 3.6.
- To run the model, hydrogeological data were entered in Section 2, transport parameters in Section 3, source zone characteristics in Section 4, and desired output information in Section 5.

KEY POINT:

The Toolkit was able to reproduce observed soil concentrations to within an order of magnitude.

The initial site estimated seepage velocity of 20 ft/yr was unable to reproduce the observed plume length at the site. A better comparison between simulated and observed soil concentrations was obtained by increasing the seepage velocity, initial source groundwater concentration, low-k zone fraction organic carbon, and the diffusion coefficient. Based on the calibrated model, the Toolkit yielded a good comparison to soil core concentrations 65 ft downgradient of the source.

Note that although for this evaluation, only the seepage velocity, source concentration, low-k fraction organic carbon, and the diffusion coefficient were used as calibration parameters, there could be other combinations of input parameters could be adjusted to yield similar or better results.

After working to match the soil core data, the model now can be used to estimate future concentrations and mass discharge in the low-k zone at the site.

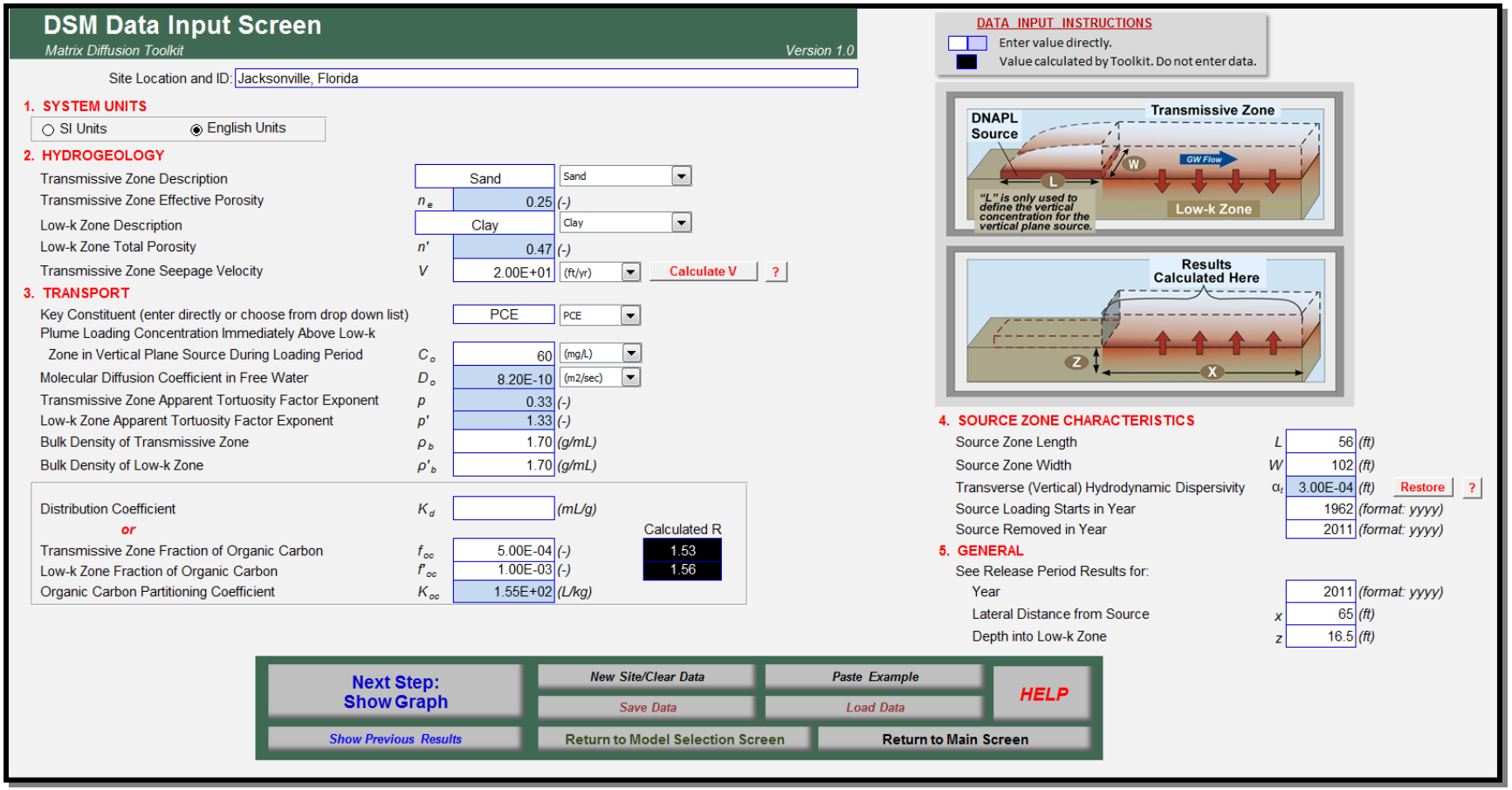

Figure 3.2. DSM Input Parameters (Initial).

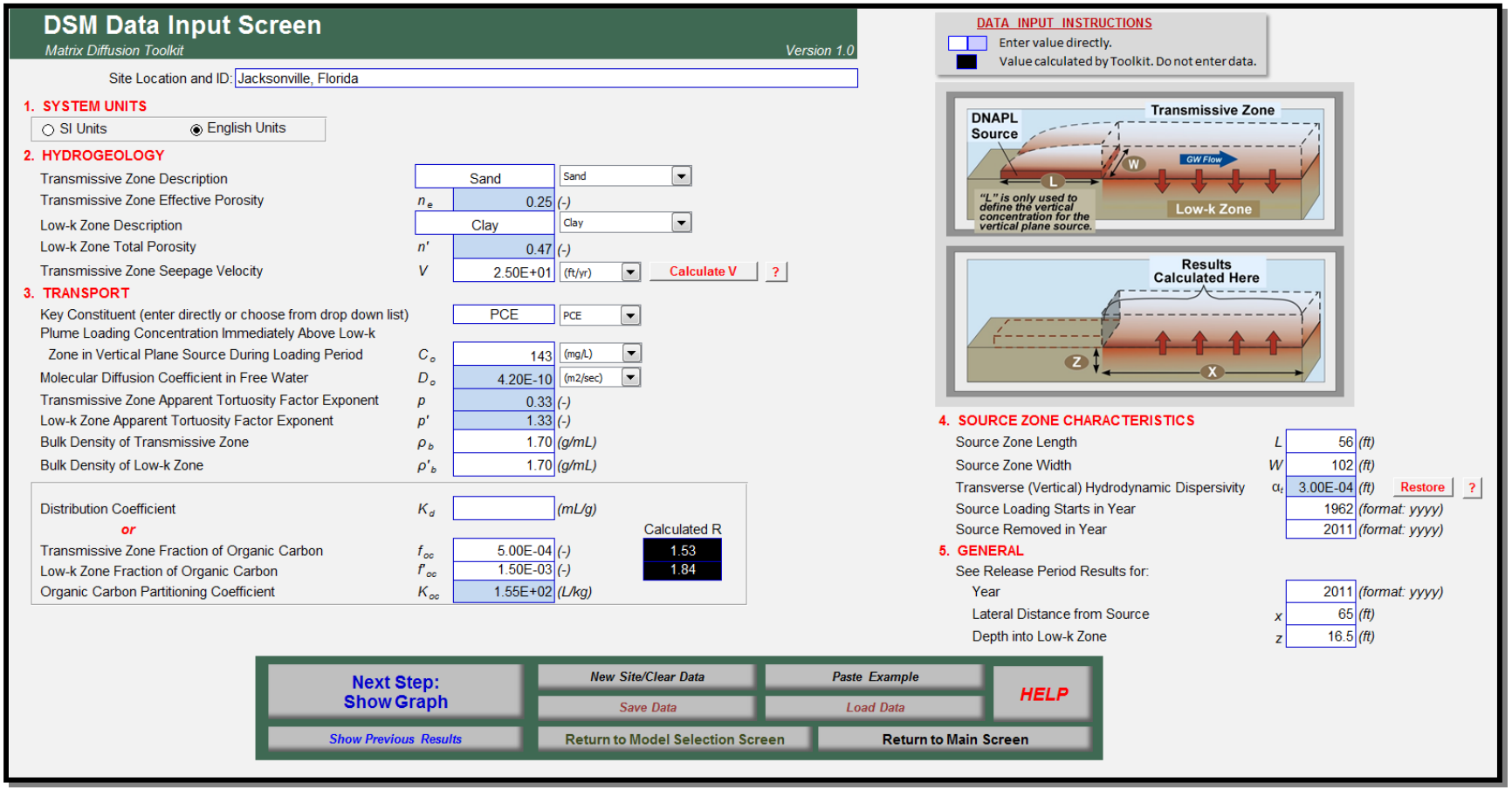

Figure 3.3. DSM Input Parameters (Calibrated).

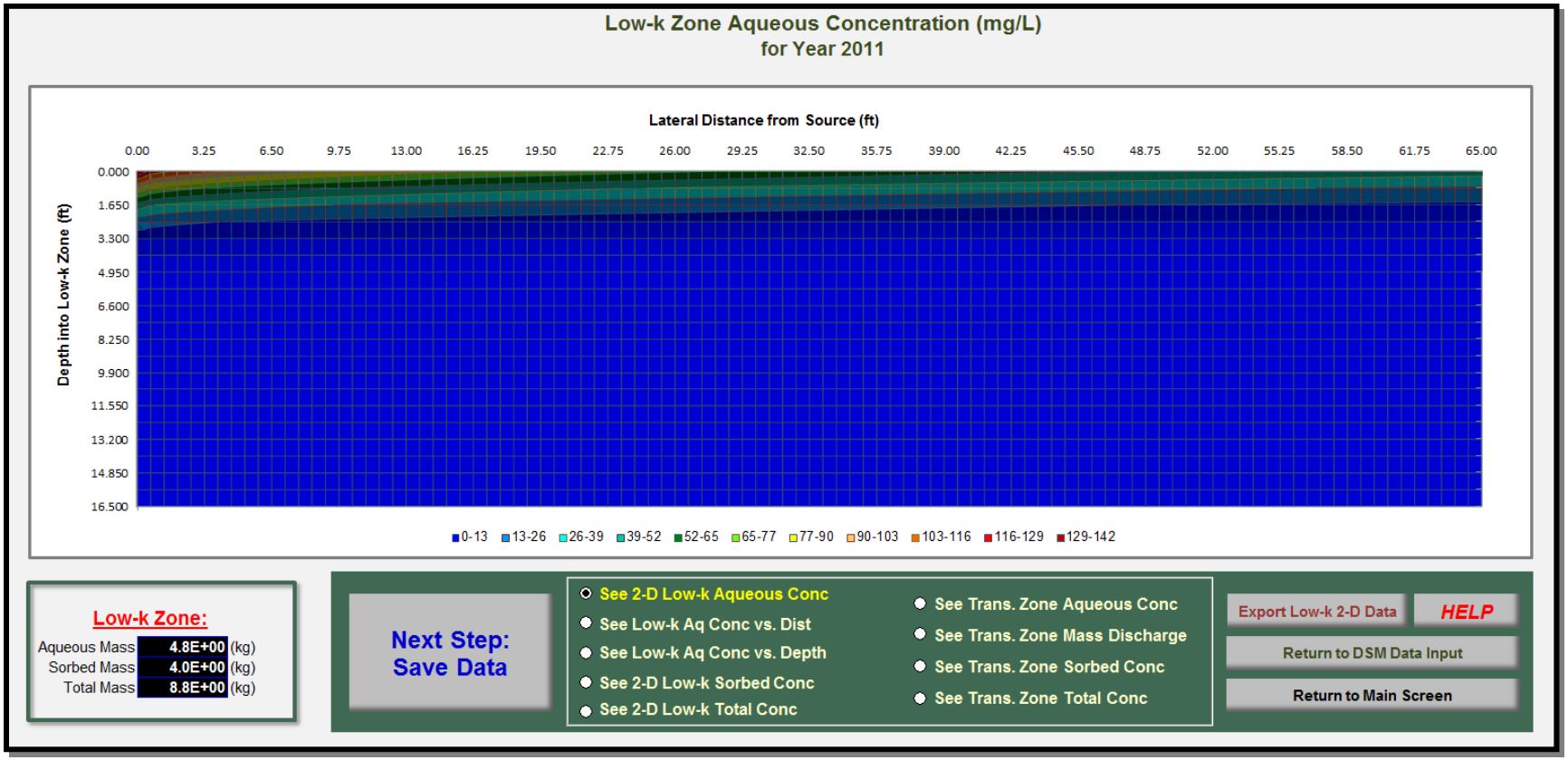

Figure 3.4. DSM Output for OU3-3 (Calibrated).

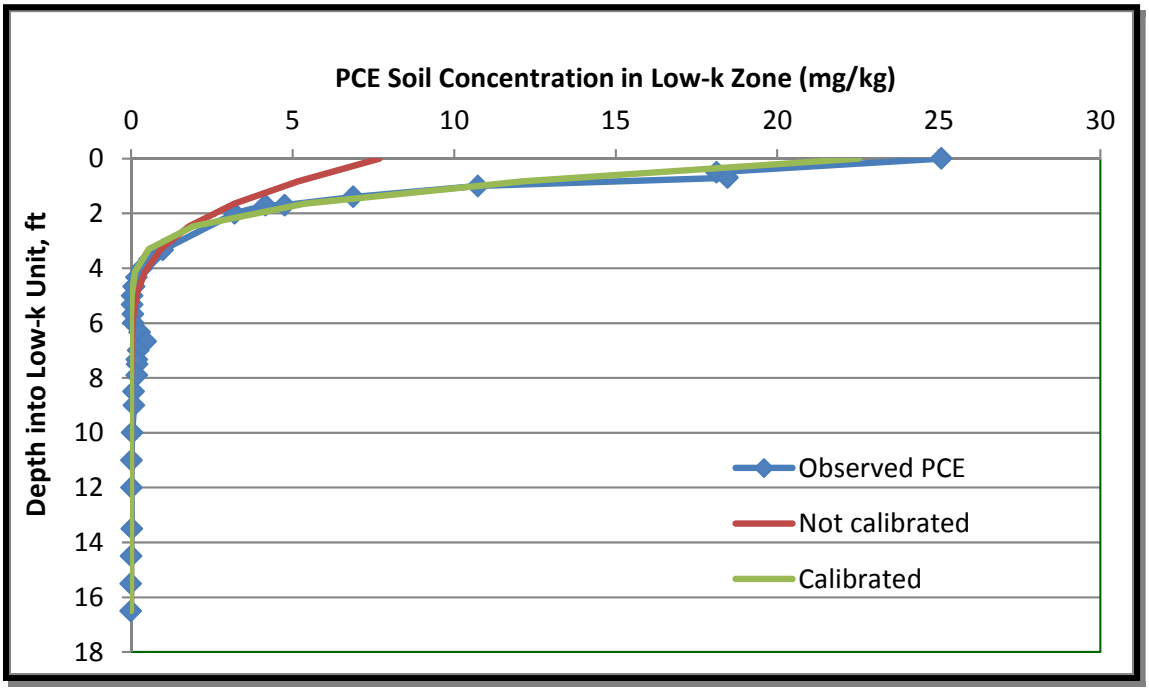

Figure 3.3. Comparison of Toolkit Simulated and Field Observations – OU3-3 (65 ft from Source). Note the red line did not calibrate well due to the low seepage velocity estimate for the site (see text). This point was then calibrated using a larger seepage velocity. The match between actual and modeled results is very close.

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